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A COMPARATIVE STUDY OF ETCH-FIGURES. THE AMPHIBOLES AND PYROXENES.

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INTRODUCTION.

AMONG the larger groups of rock-forming silicates, there is none perhaps which, in the present state of our knowledge, offers more difficulties in the determination of systematic relationships than the amphibole family. Its importance for the petrographer needs no emphasizing here, yet it is he who has to meet the difficulties of classification and discussion under the most disadvantageous circumstances; in general, by reason of its association, the amphibole of an eruptive rock or of a crystalline schist lacks crystal form, and, because of numerous inclusions, it may often be impossible to procure a reliable chemical analysis of the mineral. Thus deprived of two principal aids to diagnosis, the worker in rock-forming amphiboles must make the most of the other criteria which offer themselves. In so doing, he may eventually be able to repay the pure mineralogist for his services to the study of the crystalline rocks and present new considerations that can lead to the interpretation of the mineral species as such without relation to rock genesis or rock classification. Of the methods which, so far, have been almost completely neglected by petrographers in the investigation of amphiboles, is that of the use of etch-figures on planes of the more important zones. I propose in the following pages to record briefly certain results I have obtained while breaking ground in this new field of inquiry.

The first, and so far as I have learned, the only published reference to actual experiments in etching an amphibole, occurs in Bořický's first essay on microchemical methods.* Plate II. Fig. 7 of his work represents a hornblende etched with fluosilicic acid on the clinopinacoid. The reference in the text to this drawing was occupied with the mention of the chemical reaction, and especially of its products, — nothing further.

* Archiv d. naturw. Landesdurchforschung von Böhmen, III. Prague, 1877.

Sir David Brewster observed his "Optical Figures" on a few hornblendes characterized by natural pits of corrosion.* Since nothing has been done towards a comparative review of etching phenomena with respect to the amphiboles, I shall state some of the reasons why the present research was begun.

(1) In the first place, it has been considered a good opportunity to test once more how far etch-figures are dependent on the method of attack, and to devise a convenient and uniform method for the group in question. (2) Will the etching process furnish any information as to the attackability of amphiboles in hydrofluoric acid? (3) Are the etch-figures variable in shape with the chemical composition of the mineral? Will they throw any light on the problem of isomorphism among the amphiboles? (4) Will the amphibole figures by comparison with those on the corresponding faces of pyroxene, tend to strengthen the parallel between the two mineral groups? (5) Can cleavage pieces and crystals of amphibole be crystallographically oriented by means of etch-figures? (6) Will the latter give us any data on the vexed question of the best standard orientation of amphiboles as a whole? Is Tschermak's or Nordenskiöld's recommendation better fitted to disclose the many varied relationships of the group? (7) Are the amphiboles holohedral? (8) Are anthophyllite and gedrite really orthorhombic? (9) Incidentally, in connection with the attempt to solve these problems, I have compared etch-figures using hydrofluoric acid with those obtained with the corrosive alkalis.

Now, in order to pave the way for a concise description, and perhaps readier understanding of the following discussion, a few lines may be taken to define a certain number of terms which have been introduced with more or less technical import. Several of these are literal or slightly modified translations of the valuable German names or phrases of Becke, Baumhauer, Leydolt, and others.

The etch-figure itself may be a cavity of corrosion, an "etch-pit" ("pit of corrosion," Aetzgrübchen, Aetzvertiefung), or it may be an etch-hill (Aetzhügel), a residual boss standing up in relief above the general surface of the crystal. Either etch-pit or etch-hill is bounded by "figure-faces" † (Aetzflächen), in general manifestly plane, sometimes

* Phil. Mag., 1853, Vol. V., p. 16.

† Molengraaf's nomenclature seems unfortunate in relegating the short, useful word "Aetzfläche" to the comparatively unimportant curved surface which often truncates a crystal edge when exposed to corrosive agents, and compelling us to speak of the figure-face of a pit as an "internal etch-face" (innere Aetzfläche). — Zeit. für Kryst., 1888, Bd. XIV. p. 174.

apparently curved, faces. Many pits normally exhibit a figure-face parallel to the plane etched; it may be designated the "bottom-face." An "etch-zone" is a zone containing two or more figure-faces ("Aetz-zone" of Molengraaf, not equivalent with the "Aetzzone" of Becke). The periphery of the pit where its figure-faces intersect the plane attacked is here called the "outline" of the figure, and each "edge" that composes it may thus be a straight or curved line as its figure-face is plane or curved. A "corner" is the point where the etched plane and two adjacent figure-faces meet.

As the process of etching continues, a pit usually increases in size, often (depending partly on the symmetry of the etched plane) changes in shape of outline, and, in many cases, deepens as the result of replacement of early formed figure-faces by others of different indices, accompanied by the necessary "diminishing" of the "bottom-face" if there be one present (cf. pits on apatite, calcite, galenite, gypsum, zinc-blende, etc.). These changes in the figures *may* be continuous, but often have rather the look of being intermittent, the replacement of one figure-face by another taking place as a momentary change, faces of intermediate indices not appearing at all. The first stage of development of a pit may be called its "initial" form. The development ends where the outline begins to be seriously impaired by the solution of the surrounding part of the etched surface. Just preceding this point in the history, the pit may be called "mature," and the process intervening between the initial and mature stages is that of "maturing." Von Ebner's "instantaneous" and "retarded" types are connected by transitions, but are not easily to be compared to "initial" and "mature" figures, since his types refer simply to the length of time required to develop the pits, and are not restricted to the use of one solvent.*

DISCUSSION OF ETCH-FIGURES IN THE MICROSCOPE.

It is believed that a description of the etch-figures as seen in reflected light with vertical incidence would be, on the whole, of more value than an account of the same figures examined under other conditions (transmitted light, Lichtschimmer). Within certain limits, this method is easily carried out with the aid of the modern appliances to be found on the large models of most petrographical microscopes, and thus a new etch-figure can in a few minutes be compared in its main features with

* Sitzungsber. der Akad. d. Wissen., Vienna, 1885, Bd. XCI. p. 775

those already established for the corresponding face and mineral group, or with analogous figures belonging to other species. Furthermore, such a description may be made in cases where any determination of the indices of the figure-faces is impossible on account of the absence of "Lichtschimmer," due to various causes, as fibrosity, minuteness of figures, curvature of the surface studied, etc. But it is necessary to recognize that a complete analysis of a figure is not possible in many cases, even under the most favorable circumstances. This is true, for example, of the pits on the prismatic faces of amphibole and in the vertical zone of most monoclinic minerals. Relatively low powers of the microscope must always be used, since contrasts of dark and light are speedily lost above 200 diameters, and thus it often cannot be decided whether an apparently rounded figure-face may not really be one compounded of many small faces, according to the well known examples of Becke, Baumhauer, and others. Hence, inasmuch as it is not practicable to determine in the microscope the elements (faces, angles, symmetry, etc.) with the same precision and detail with which we can define a crystal, it becomes advisable to choose certain elements of the figure that are sufficient to fix its general shape. Such elements will be those which can be directly measured in the microscope and with a maximum of exactness. They will include straight sides and the angles between them as well as the special angles between curved sides characteristic of each figure. These elements, too, had best be such as can be recognized on very small figures of a given category, since in some varieties it may be feasible to produce figures only relatively very minute. Lastly, we must have a base-line of reference for all measurements; — in amphiboles, there is an excellent one, the trace of the cleavage, which generally makes it unnecessary to search out the directions of edges bounding the crystal-face.

For the convenient examination of figures on (110), it is well to use prisms with sides as smooth as possible, so that the mineral will lie flat, and the plane to be studied perpendicular to the axis of the microscope. In the study of terminal planes, or of material with which such perfect prisms are not obtainable, the crystal or cleavage piece may be readily brought into the desired position by mounting it on an object-glass with wax and then adjusting it so that the simultaneous reflection of a ray of light from the glass and the plane may occur. With lustrous faces, this adjustment can thus be carried out with a close degree of accuracy.

The microscope used was a Nachet, provided with an apparatus for vertical incidence of the light that illuminated the crystal-face. The light was led through a collimator attached to an Auer lamp. Below

the collimator, the metal casing of the lamp was pierced so as to allow of a source of transmitted light for getting extinctions in cleavage plates. Orientation could thus be effected by means of extinction (when the amphibole was known), as well as by using terminal planes.

For reasons explained further on, Tschermak's orientation is adhered to throughout this paper ($\beta = 73^\circ 58'$).

The photographic illustrations I owe to the skill of M. Monpillard of Paris. The difficulties in reproducing anything like the sharpness of the etch-figures on amphiboles, especially on faces other than that of the fresh cleavage flake, are very great and fully explain any lack of definiteness that may be observed in the micro-photographs. The diagrammatic figures were drawn by means of a camera lucida and bring out more clearly than the photographs, the points of essential resemblance and dissimilarity which need emphasis.

Both in the diagrammatic figures and the wash-drawings of Plate I. the cleavage trace on each etched surface is represented by a straight line, which the reader will immediately recognize. This line is replaced in the photogravures by the longer edge of the page. The top of the crystal will as usual be directed toward the top of the page in the case of planes in the vertical zone; the front of the crystal toward the bottom of the page for terminal planes.

MATERIALS OF STUDY.

The work the results of which are embodied in the following pages was begun in the laboratory of Professor Rosenbusch at Heidelberg, where the initial experiments were carried on with crystals of Vesuvius hornblende obtained from the collection of the Mineralogical Institute, and with Zillerthal actinolite, St. Gothard (?) tremolite, and Bohemian hornblendes from the private collection of Professor V. Goldschmidt of Heidelberg. To this material were added 41 specimens from the Imperial Museum, Vienna, through the kindness of Professor Berwerth, some 20 others from the collection at the Jardin des Plantes, Paris, due to the liberality of Professor Lacroix, six fine crystals of aenigmatite and arfvedsonite from Professor Ussing, Copenhagen, classic glaucophane from Professor Barrois, Lille, and much American material from Professor Hobbs, Madison. To these gentlemen I should like to express my hearty thanks for the privilege of securing so many specimens with little trouble to myself, — material which in many cases is classic, and of considerable value from the mere monetary point of view. Without the use of so many representatives of the group, I should not have felt

enough confidence in the generalization from certain types to all types. The systematic investigation was almost entirely pursued in the laboratory of Professor Lacroix, and I desire to acknowledge, in particular, his generosity in placing at my disposal the apparatus necessary for the etching.

The list of specimens is self-explanatory. For convenience I have followed Dana's classification closely, without however implying an absolute adherence to all its details. I have inserted the catalogue numbers of the Museum specimens, sometimes the date of collection, and, where possible, leading references to original papers in connection with those specimens that have furnished particular descriptions or material practically identical with them. An asterisk denotes a specimen *presumably* similar to the classic material from the same locality. The source of each specimen is indicated in the general list by letters prefixed to the number corresponding. H. = Heidelberg, V. = Vienna, P. = Paris, C. = Copenhagen, M. = Madison, L. = Lille.

Amphiboles proper.

A. Orthorhombic amphiboles.

a. Anthophyllite.

P. 1. Kongsberg, Norway : —

Des Cloiseaux, *Nouv. Recherch.*, 1867, p. 541.

Michel Lévy and Lacroix, *Min. des Roches*, 1888, p. 149.

P. 2. Nunangiaast, Greenland. — 20-125.

P. 3. Regardsheim, Norway.

b. Gedrite.

P. 4. Gèdres, France : —

Dufrénoy, *Ann. des Mines*, 1836, Vol. X. p. 582, etc.

B. Monoclinic Amphiboles.

a. Non-aluminous.

(1) Tremolite.

H. 5. St. Gothard (?).

P. 6. Siberia. — "Grammatite." — 2-855.

P. 7. Faroe Islands. — 64-63.

V. 8. Newport, Bucks Co., Mass. (?) A. c. 4154.

*M. 9. Gouverneur, N. Y.

(2) Actinolite (with certain allies).

*H. 10. Zillerthal.

*P. 11. "

P. 12. Syra.

P. 13. Gellivara, Asia Minor, 68-31.

V. 14. Killaersarbik, Greenland. A. e. 924, 1818.

V. 15. Anaitsirksarvik, Greenland. A. u. 98.

*V. 16. Orange Co., N. Y. E. 5606, 1888.

V. 17. Arendal, Norway. A. e. 961, 1825.

- V. 18. Ottawa River, Canada. A. e. 968, 1826.
 P. 19. (Smaragdite), Greenland.
 *V. 20. (Richterite), Langban, Sweden. A. a. 509.
 *V. 21. " " " G. 3122, 1894.
 *V. 22. (Astochite), " " G. 4080, 1895.
 (3) Cummingtonite.
 *M. 23. Cummington, Mass.
 (4) Grunerite.
 P. 24. Collobrières, Dep. du Var, France : —
 Lacroix, Bull. Soc. Min., 1886, p. 40.
 Minéraux des Roches, 1888, p. 144.
- b. Aluminous.
 *P. 25. (Edenite) Edenville, N. Y. 64-145.
 *V. 26. (Pargasite) Pargas, Finland. A. e. 928, 1848.
 V. 27. " " " A. o. 469.
 Berwerth, Sitzb. Akad. Vienna, 1882, Bd. LXXXV. p. 158.
 *V. 28. (Pargasite). A. e. 929, 1826.
 V. 29. (Carinthine) Saualpe, Carinthia. A. o. 464 and 465.
 Tschermak, Min. und Petrog. Mittheil., 1871, p. 38.
 *H. 30. (Syntagmatite of Breithaupt), Vesuvius.
 *V. 31. Kragerö, Norway. G. 3287, 1894.
 V. 32. Arendal, Norway. A. f. 2., 1827.
 V. 33. " " A. e. 967.
 V. 34. " " A. e. 891 and 892.
 V. 35. " " A. e. 897.
 V. 36. " " A. e. 898.
 V. 37. " " A. o. 432.
 V. 38. " " A. o. 434.
 V. 39. " " A. f. 3, 1824.
 V. 40. Norway. A. o. 450.
 V. 41. Philipstad, Sweden. A. o. 458.
 *V. 42. Kafveltorp, Sweden. 1889.
 *V. 43. Wolfsberg, Bohemia (in basalt). A. a. 1860.
 V. 44. Orbus, Kupferberg, Bohemia. A. o. 446.
 *H. 45. Bilin, Bohemia.
 V. 46. Mayenegg, near Kupferstein. B. e. 5378, 1838.
 V. 47. Easton, Pennsylvania. A. e. 971, 1826.
 V. 48. Worthington, Mass. A. e. 902, 1825.
 V. 49. Kangerotvarsvik, Greenland. A. e. 922, 1818.
 V. 50. Edenville, N. Y. (greenish-black). A. e. 913, 1829.
 V. 51. " " (dark green). A. e. 901, 1827.
 V. 52. Gebel Gharib, Arabia. B. d. 6369, 1877.
 P. 53. (Gamsigradite) Gamsigrad, Servia. 97, 351.
 Lacroix, Bull. Soc. Min., 1887, Vol. X. p. 147.
 *V. 54. Wolfsberg, Bohemia (twin). F. 3850, 1890.
 P. 55. Riveau Grand, Mont Dore.
 Lacroix, Minéralogie de la France, 1893-95, Vol. I. p. 663.

Glaucophane.

*P. 56. Ile de Groix.

L. 57. " "

Barrois, Am. Soc. Géol. du Nord, 1883, p. 19.

P. 58. Oulx, Savoy.

*P. 59. (Gastaldite) Champ de Praz, Val d'Aosta. 90, 197.

Crossite.

*P. 60. Berkeley, Cal.

Riebeckite.

P. 61. St. Peter's Dome, Colorado. 89, 6.

Arfvedsonite.

*P. 62. Kangerdluarsuk, Greenland.

*C. 63. " "

(Barkevikite.)

*P. 64. Barkevik.

Aenigmatite.

*P. 65. Nauyasakik, Greenland. 95-190.

*C. 66. " "

Bronzite.

*P. 67. Kraubat, Styria.

P. 68. Greenland. 9-25.

Hypersthene.

P. 69. St. Paul's Island. 35-2631.

Lacroix, Min. des Roches, 1888, p. 261.

Diopside.

*P. 70. Ala.

Augite.

P. 71. Puy de la Rodde.

Gonnard. Cf. Lacroix, Minéralogie de la France, Vol. 1, p. 578.

Fowlerite.

*P. 72. Franklin, New Jersey.

METHODS USED.

The researches of recent years on figures of corrosion have shown that the most fruitful results are obtained by quantitative methods, that is, by the use of reagents under definite specified conditions, and by close measurement of the figures. It hardly needs mention that there is much yet to be learned regarding the cohesional properties of the species belonging to each of the great mineral groups, as well as regarding the similar relations which may exist between corresponding members of two different families. Just as we may describe as accurately as possible the hardness or the fusibility, the specific gravity or the optical properties, of a species, not only to fix it as an independent type, but also to relate it to the other members of its own family and to other mineral groups, so we believe it is possible to construct with

some precision a scale by means of which crystal faces may be defined as to molecular cohesions. This has, in fact, been accomplished in certain cases; but, in general, etch-figures have only been used *qualitatively*, so to speak, and as yet there has been not enough of continuity of method from one investigation to another to make possible detailed comparison of species with species in this matter of facial cohesion. In the particular case of the group here considered, it has seemed desirable to make it possible to reproduce the conditions finally selected for etching, so as to permit of the discussion of new amphiboles with the aid of data already in hand. May it not be possible that the contradictory results of certain observations is simply due to difference in methods? Thus, Penfield, Meyer, and Bömer found the basal plane of quartz characterized by etch-hills when hydrofluoric acid was used,* while with the same solvent Gill obtained pits of corrosion.† For these and other reasons noticed below, I have tried to establish a constant method which would give good results with all varieties of the great amphibole family, and one which can be extended to the pyroxenes and other silicates. That such a method be wrought out, it was necessary that some preliminary experiments should be made, for reasons, some very obvious, others less so, all of which I shall summarize in this connection.

1. It is generally advisable to choose prominent crystal-faces, usually those of simple indices and those parallel to cleavages. That one would select such faces is to be expected, but I think this point should be especially in mind if comparisons are to be made as widely as possible. An advantage in choosing cleavage pieces or the corresponding crystal-face is evident in those groups where certain members appear only as allotropic individuals in rock aggregates. Even in these cases, their etch-figures may be produced on a good cleavage when figures on other planes would only be possible on artificial faces. Fortunately, too, for the discussion of rock-forming amphiboles as well as of the group as a whole, the cleavage pieces give the sharpest and most regularly developed figures to be obtained on any given crystal.‡ The prismatic cleavage of amphiboles has thus a superior claim to attention, and I have accordingly laid most stress on this important face in the course of the present investigation. Next to these, pinacoids will naturally give the most useful

* Trans. Connecticut Academy, 1889, p. 157. Neues Jahrb. für Min., etc., 1891, Beil. Bd. VII. p. 534.

† Zeit. für Kryst., Bd. XXII. p. 111.

‡ Cf. Baumhauer, Resultate der Aetzmethode, p. 3.

results. As a matter of fact, I have found (010) and (100) to be among the interesting faces for etching on amphiboles. Moreover, not only are they very common planes; they are also those most likely to reveal the fundamental features of crystal structure.

2. Since the production of etch-figures on a bisilicate is in large part the result of a chemical reaction between mineral and solvent, it is clear that the figure will, in every case, depend on the chemical nature of both. Two varieties apparently isomorphous and differing little in composition may afford figures markedly different from each other, although produced on planes with the same symbols and with the same solvent. Examples will be noted in the sequel. Such being the fact, it is natural to conclude that the figures shall be similarly sensitive to small changes in the solvent also.* A striking illustration is to be found in the series of etch-pits formed on (010) of actinolite by hydrofluoric acid in various states of dilution in water or mixture with sulphuric acid. There is a steady change in the orientation of the figure as the state of purity of the hydrofluoric acid is affected. Details concerning this phenomenon are given in the section devoted to a description of figures on (010).

I chose hydrofluoric acid as the universal attacking reagent on account of its convenience and efficiency. Inasmuch as its working depends on the degree of concentration of the acid, it becomes necessary to fix on some particular grade of acid. A number of trials soon convinced me that the concentrated commercial water solution is for general purposes the best. Not needing special preliminary preparation, it is easily obtainable in any desired quantity; experiment showed that it gave the most satisfactory figures just as the alums afford the best results with the solvent in an active state.† There is one danger to be guarded against, namely, the loss of concentration with prolonged heating of the acid; hence the advantage of easy renewal of the reagent.

Temperature and its function, the duration of immersion, are now well established to have a strong influence on the process and effects of etching. A new variable must thus be considered. As a result of a large number of trials made both incidentally and with this distinct purpose in mind, I found that good figures could be produced at many different temperatures; thus, Zillerthal actinolite will yield well developed pits of corrosion when boiled one minute in HF, or at three minutes in HF

* Cf. Von Kobell, *Sitzungsber. Münchner Akad.*, 1862, p. 199; Ben Saude, *Ueber den Perowskit*, Göttingen, 1881; Meyer, *Neues Jahrbuch*, 1883, Bd. I. p. 77.

† Klocke, *Zeit. für Kryst.*, 1877-78, Bd. II. p. 130.

on a water bath, or, again, when immersed several hours in cold HF. Among all these possibilities I have endeavored to secure for all comparative studies a temperature as nearly constant as possible, and this for two reasons. In the first place, it would not be at all certain without direct proof that the figures with any one reagent remain constant for all temperatures. Bömer discovered that the form and orientation of the figures on quartz produced by attack with HF were affected by the temperature of the reaction.* It is reasonable to suppose that temperature may have a corresponding effect on amphibole figures when the same reagent is used. As will be noticed elsewhere, I have been able to determine no sensible variations in figures on (110) from this cause, but it cannot be denied that they are present. Secondly, I wished to tabulate the amphiboles with reference to their power of resisting solution in the etching process. The standard temperature chosen for these reasons is that of the water bath, one that is nearly constant, attained with no difficulty, and found to suit the necessities of the case very well.

To secure a standard temperature for the reaction repeatedly and expeditiously demanded in addition a certain amount of arbitrary treatment, since the amount and initial temperature of the acid have not yet been allowed for. A platinum crucible of the usual slightly conical form and with a diameter at the bottom of about 4 cm. is filled to a depth of 1 cm. with the cold acid; the mineral, resting in a platinum net, is immersed, and at the same time the crucible is placed 1 cm. deep in the steam of a water-bath which is kept constantly at 100 degrees Centigrade. The attack is readily checked at any moment by lifting the platinum net and plunging it with the mineral into water. The coating of fluorides could be readily removed by brushing the mineral in running water, or by dissolving them in hot concentrated hydrochloric acid.

Another point of inquiry in connection with formation of an ideal method would be the effect of increasing the energy of the reaction by the agitation of the acid during attack. Klocke, in his classic research on the alums, found that on agitating the solution in which corrosion pits were forming, the figures grew larger rapidly, due, as he stated, to the dissipation of the "Hof" (Lösungshof) of liquor near the figure which had become laden with the products of solution.† Experiment of the same kind was carried on with basaltic hornblende, but no material improvement was effected on the sharpness of figures produced without

* Neues Jahrbuch, 1891, Beil. Bd. VII. p. 538.

† Zeit. für Kryst., 1877-78, Bd. II. p. 298.

agitation. I am inclined to think that convection currents in the warmed acid are sufficient to perform the same function.

In thus fixing on a universal solvent, its temperature, state of concentration and of convention, we have narrowed down the variables of the process to one, the duration of attack. This facility in arriving at the conditions of a uniform method of etching is not possible when the caustic alkalies are employed and hence these will be referred to only incidentally in the following pages. Unless the contrary be stated, the standard conditions of etching are to be understood in every experiment.

THE OPTIMUM EXPOSURE OF THE DIFFERENT SPECIES.

Here the study was confined to cleavage pieces. It was naturally found that as the figures increased in number, they also increased in size, any changes in shape not being sufficient to remove them from the category of "primary" figures (Becke). In most cases, the general cleavage surface showed no serious roughening as the figures grew and the attack was allowed to continue nearly to the point where overlapping of the pits (generally aggregated in groups) would occur. This length of exposure usually gave the best figures for study; hence I have called it the "optimum" duration of attack. Since the determination of the optimum length of immersion was a matter of considerable labor, the result of several trials with almost all varieties, I have thought it worth while to tabulate the results obtained with a certain number of specimens. It is to be understood that the following table is only approximately accurate. Perfectly fresh acid was not used in every case, and, of course, the longer the acid remains on the water bath, the weaker it becomes; moreover, the amount of steam in the water bath is variable to some extent, and thus the HF might become heated at different rates. Care was taken to allow for such causes of variation from the true optimum.

Optimum Exposures.

| | | |
|------------------------|---------------|---------------------|
| Anthophyllite. | P. 11 | 2½ minutes. |
| P. 1 | P. 12 | 2½ " |
| P. 2 | P. 13 | 1 " |
| Gedrite. | V. 14 | 4 " |
| P. 4 | V. 15 | 1½ " |
| Tremolite. | V. 16 | 2 " |
| H. 5 | V. 17 | 2½ " |
| V. 8 | V. 18 | 1 " |
| Actinolite and allies. | P. 19 | 1½ m. (Smaragdite). |
| H. 10 | V. 20 | ¾ m. (Richterite). |

| | |
|---|--------------------------------------|
| V. 21 $\frac{3}{4}$ m. (Richterite). | V. 44 $\frac{1}{4}$ minutes. |
| V. 21 $1\frac{3}{4}$ m. " (another specimen). | V. 46 $2\frac{1}{2}$ " |
| V. 22 1 m. (Astochite). | V. 48 3 " |
| Common and basaltic Hornblende. | V. 49 2 " |
| P. 25 $2\frac{1}{2}$ m. (Edenite). | V. 50 1 " |
| V. 26 $2\frac{1}{2}$ -3 m. (Pargasite). | V. 51 1 " |
| V. 27 " m. " " | V. 52 $\frac{3}{4}$ " |
| V. 28 " m. " " | P. 53 1 (Gamsigradite). |
| V. 29 2 m. (Carinthine). | Glaucophane. |
| H. 30 $\frac{1}{2}$ m. ("Syntagmatite"). | P. 56 2 minutes. |
| V. 31 $1\frac{1}{2}$ minutes. | P. 58 (?) $1\frac{1}{2}$ " |
| V. 32 $1\frac{3}{4}$ " | P. 59 $1\frac{1}{2}$ " |
| V. 33 $1\frac{1}{4}$ " | Riebeckite. |
| V. 34 1 " | P. 61 $\frac{3}{4}$ " |
| V. 36 $\frac{1}{3}$ " | Arfvedsonite. |
| V. 37 $\frac{1}{2}$ " | P. 62 $\frac{1}{2}$ " |
| V. 39 1 " | (Barkevikite). |
| V. 40 1 " | P. 64 $\frac{1}{2}$ " |
| V. 41 $1\frac{1}{2}$ " | Aenigmatite. |
| V. 42 1 " | P. 65 $\frac{1}{3}$ " |
| V. 43 $2\frac{1}{2}$ " | C. 66 $\frac{1}{3}$ " |

The average optimum exposure of these groups as indicated by the optimum exposure can, then, be expressed somewhat as follows:—

| | |
|--|------------------|
| Anthophyllite | 2 minutes. |
| Gedrite | 2 " |
| Tremolite | 3 " |
| Actinolite | 2 " |
| Richterite | 1 " |
| Astochite | 1 " |
| Edenite | $2\frac{1}{2}$ " |
| Pargasite | $2\frac{3}{4}$ " |
| Common and basaltic hornblende | $1\frac{1}{4}$ " |
| Glaucophane | $1\frac{3}{4}$ " |
| Riebeckite | $\frac{3}{4}$ " |
| Arfvedsonite | $\frac{1}{2}$ " |
| Barkevikite | $\frac{1}{2}$ " |
| Aenigmatite | $\frac{1}{3}$ " |

ATTACKABILITY OF THE AMPHIBOLES.

Referring as they do to the appearance of best figures on the prismatic cleavage, without regard to their size, these tables do not express the attackability of the various species. Thus the average time for the development of the sharpest figures on anthophyllite and actinolite is in

each case, two minutes, yet the actual amount of material carried off in solution from the very minute pits of the anthophyllite is extremely small when compared with that removed in the process of excavating the much larger pits on the monoclinic mineral. While working out optimum exposures, I generally had opportunity to observe the incipient stages of attack on cleavage-cracks and of the roughening of the whole surface of the crystal. In this way a general impression of the relative attackability of these minerals was gradually made upon me. I give the series for what it is worth, beginning with the varieties most resistant to hydrofluoric acid, and naming the others in order of less resistance: — 1. The orthorhombic amphiboles. 2. Actinolite. 3. Tremolite. 4. Glaucophanes. 5. The light-colored aluminous monoclinics. 6. The common green hornblendes. 7. The basaltic hornblendes. 8. The Richterites. 9. Arfvedsonite. 10. Riebeckite (?). 11. Aenigmatite. It will be seen that the resistance to solution decreases with increase in soda and in sesquioxide of iron.

But not only are the differences of attackability due to differences in chemical composition and crystal system, they are also strongly affected by physical conditions irrespective of species. The physical influences may entirely mask the attackability resulting from the chemical reaction alone. The theories which have been made to explain the irregular distribution of etch-figures on a given plane by corresponding irregularities in the grouping of the chemically active part of the solvent in use, can have no application to many cases that have come under my notice during the course of the present research. They are often rather to be explained as dependent on a loosening of the original molecular structure of the mineral by mechanical action without at the same time being accompanied by chemical decomposition. The presence of submicroscopic cracks or planes of parting (a superficial capillary zone) will necessarily give the acid greater surface by which to attack and permit of a readier dislodgment of the molecules from the grip of physical cohesion. A good analogy is found in the hardness of certain pseudomorphs; manganite with a hardness of 6 forms a pseudomorph after polianite (pyrolusite), but has then an apparent hardness of only 3.

A few typical examples of this differential resistance to solution will suffice for our present purpose. Two intergrown crystals of V. 42 apparently of equal freshness, each bearing the plane (011), were simultaneously immersed for several periods and examined at the end of each interval for the relative progress of attack. The plane (011) of one crystal was seen to have been affected decidedly *sooner* than the same

plane of the other. In this case, the ready yielding of the former may have been caused by its being exposed to more active convection currents than the second crystal, due to position in the acid. But this explanation cannot apply to V. 46, where the optimum exposures for cleavage flakes from different crystals, though from the same hand specimen, varied from two and one half to five minutes, and the pits were of nearly equal size (area and depth) on all the pieces. V. 34 afforded some light on the question in the behavior of two terminated crystals, the (011) of the one, less lustrous than the same plane of the other, was the more rapidly attacked. The suggestion that the phenomenon is a result of alteration can hardly be avoided. That the alteration may be an almost, if not quite, exclusively physical one and not associated with a serious change in the original chemical molecule of the hornblende, seems clear from the facts observed in an experiment on V. 31. The hand specimen is a "Krystallstock" composed of well defined individuals, tipped with asbestos and occasionally showing patches of an asbestiform substance on the sides of the crystals. At two minutes' exposure, one of these gave sharp but relatively few figures on (110) near the point of attachment at the end of the crystal. The other three fourths of the surface of the prism was characterised by the appearance of numerous cleavage cracks which gradually increased in number in the direction of the free (in the druse unattached) end, and there was a simultaneous increase in the number of pits. The development of the latter was independent of the asbestiform patches, and, from the uniformity of color of the general surface, I have concluded that there has not been chemical decomposition sufficient to explain the differing rates of etching. It may be noted that the much attacked end was directed *upward* in the acid, and any heating by direct contact with the platinum at the bottom of the crucible would tend to dissolve the unaltered extremity of the crystal the more rapidly.

As a general rule, the crystal-face (110) was observed to be less resistant to solution than the parallel cleavage plates of the same individual crystal, but the converse was often true.* Thus at one and two thirds minutes, the cleavage showed much stronger attack than the corresponding crystal surface (110) of a specimen of V. 32, although here again the original face was facing downward, the cleavage plane upward, in the acid solution. The mineral was perfectly fresh in appearance, and betrayed no alteration to the eye such as seemed best to explain the same relations characterizing other examples: e.g. V. 8, V. 14, V. 17, V. 26, V. 42.

* Cf. Becke's experience with zinc blende, *Min. und Petrog. Mitth.*, 1883, Bd. V. p. 485.

In these cases, actual separation had taken place along the cleavage planes in question long enough before the specimens were collected in the field to have permitted the physical processes of weathering to destroy to some extent the original cohesion of those layers of the crystals, while, for some reason (probably the protection of surrounding minerals), the crystal-face escaped such disintegration. That there may be other and more obscure physical differences which can explain the grouping of etch-figures was suggested by Baumhauer, who attributes the zonal arrangement of the pits on etched fluorites to them rather than to chemical variations in the zones.* The same principle is illustrated in the explanation of "Aetzgräben," † linear aggregations of pits following directions of weak cohesion control. Thus, on etched cleavage plates, there are commonly to be observed a regular grouping of figures in directions which are crystallographically fixed on hornblende; long rows of pits parallel to the trace of the second vertical cleavage, or to the trace of the rudimentary basal cleavage, without, in either case, there being actual cleavage cracks opened which would affect the etching directly. Viola has recently described the zonal distribution of pits on gypsum, the zones being regularly fixed with reference to the axis of symmetry.‡ Whether these zones represent the original stratification of molecular deposition or are the result of secondary physical change, acting on a homogeneous crystalline mass, the behavior of gypsum is another example with those already cited to show the dependence of attackability on physical cohesion, when the latter varies according to the laws of crystal structure. Incipient weathering and the development of secondary strains will favor an irregular grouping of etch-figures that are structurally accidental. These have been noticed in connection with the amphiboles. These facts lead us to suspect that Ebner's hypothesis of irregularities in the solvent can no better explain the differing attackability of a cleavage piece of calcite in its various parts than the hypothesis of varying physical conditions in the crystal itself.§

* Resultate der Aetzmethode, p. 6. Mere heating may render actinolite fibrous. See Doelter and Hussak, Neues Jahrbuch, 1884, Bd. I. p. 24.

† Ibid., p. 6.

‡ Zeit. für Kryst., 1897, Bd. XXVIII. p. 575.

§ That no *one* theoretical cause yet adduced in explanations will suffice is clear. Minute fracturings cannot, for example, pave the way for unequal etching in the case of a *growing* crystal of alum in a saturated alum solution. It is simply necessary to dilute the solution slightly in order to etch the newly made surface; here there could be no reasonable supposition that the crystal had already undergone any disintegration, yet the pits are irregularly dispersed on the surface. See

Having traced the influence of chemical composition and of physical conditions on the property of attackability, we may now proceed to inquire whether the single planes of an amphibole have different powers of resisting solution in hydrofluoric acid. I shall once more use the information gained in the process of etching; the appearance of figures and the loss of illumination using vertically incident light will be taken as the criterion of attack. Actinolite, tremolite, and common hornblende were thus examined.

A crystal of V. 42 was exposed first, 40 seconds, then one minute. At 40 seconds (111) was visibly roughened but showed no figures, while (110) remained practically intact; at the end of the second exposure *both* planes were equally provided with pits. From the mere development of figures, it would appear that (111) and (110) were of about equal attackability, but the roughening of surface gave much more reliable indications of the fact. Combining with this, the observations on the other faces, the series is correctly written in the order of increasing resistance to the

acid (111), (011) $\left\{ \begin{matrix} (100) \\ (010) \\ (110) \end{matrix} \right\}$. As a matter of fact, the maturing of pits

on the various faces often occurred at intervals so far apart as to permit of a pretty tolerable determination of the facial attackability by means of their study alone. It is essential, of course, to distinguish etch-pits from etch-hills, which may (as described by Becke) simultaneously appear on two different faces of the same crystal. A generalization was made from the study of twelve crystals of aluminous hornblendes, as follows: V. 26, V. 32 (2), V. 33, V. 35, V. 40 (2), V. 42 (3), V. 54, and P. 55. Arranging the planes in order of increasing resistance to the acid, we have, (111), (011), (130), (100), (010), (110). But what has been said about the phenomenon as affecting the corrosion on (110) applies with equal force to the other planes. With V. 54, I obtained the series (101), (010), (110), (011), in the same order as above, — an anomalous order which I could see was correlated with the lustre and general state of repair of each of the faces belonging to the crystal in question. By reason of the peculiar geological conditions, and of the position of the crystal in its druse, a prism face may suffer alteration while an end face may escape that process and the latter can thus resist an attacking acid longer, though, as we have seen, the terminal planes are regularly the ones to yield first.

Similar results were found with crystals of Actinolite (V. 16), (V. 17), and of tremolitic amphibole (V. 8). The series are, respectively, (101), (011), (100), (110), and (011), (010), (110).*

These conclusions illustrate the now well established method of interpreting molecular structure by solubility in different crystallographic directions.† The series of facial attackability correspond to the dimensional variations in the pits on the various faces of an amphibole. They explain, for example, the very general elongate form of the pits on planes of the prism zone, an elongation in a vertical sense and coupled with a greater resisting power in the prism zone itself. I may further note, in passing, that here the different zones behave, as always, in a way to indicate the holohedral character of all the amphiboles. The "Lösungsfläche" (Becke) of amphiboles is monosymmetric and centrosymmetric.

DESCRIPTION OF THE ETCH-FIGURES.

We may now proceed to the characterization of the etch-figures themselves. It has been thought most convenient, and as tending towards an easier survey of the facts, to group them with reference to crystallographic planes primarily and to consider in order the behavior of each species on etching each of these planes with hydrofluoric acid. We may hope thus to lessen the repetition of detail necessary in some degree; at the same time, the essential features of likeness or unlikeness of the different varieties will appear with most clearness. Following this more or less bald statement of fact, which is abbreviated as far as consistent with our immediate aims, there will be an attempt to correlate the facts both in way of summary review and as related to certain others which shall be especially introduced in the general discussion.

Etch-Figures on (110). Actinolite Type.

Throughout the whole series of non-aluminous amphiboles (excepting riebeckite) which I have yet studied (actinolite, tremolite, smaragdite, richterite, astochite, etc.), cleavage pieces give figures that are practically

* One fresh crystal of Zillerthal actinolite etched with an *alkali*, caustic soda, displayed greater resistance to attack on (010) than on (110). This may be another illustration of the rule enunciated by Baumhauer, that, in certain cases, the directions of rapid solution are reversed for acids and alkalies. Thus, he found it to be true for Linneite when he compared its behavior in the process of etching using nitric acid with its behavior in Becke's experiment of etching with caustic potash (Resultate der Aetzmethode, p. 20). The same holds true for magnetite (Ibid., p. 27).

† Cf. Baumhauer, Resultate der Aetzmethode, p. v.

indistinguishable from one another. They are the same as those on the corresponding crystal-face and are, so far as observed, uniform in characters for all strengths of acid and times of exposure. This does not imply that there are no differences in the figures, but these are so minute as, in most cases, to defy measurement. Since I obtained the largest and best pits on actinolite, I shall call theirs the "actinolite" type of etch-pit.

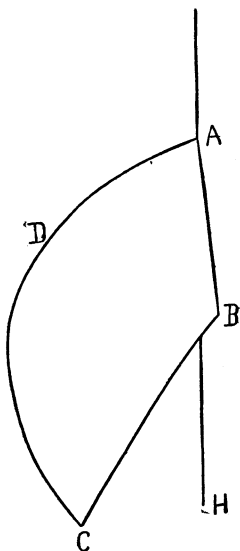


FIGURE 1.

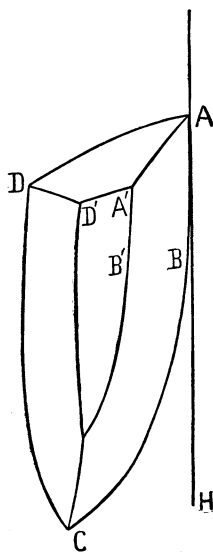


FIGURE 2.

In the diagrams (Fig. 1), (Plate I. Fig. 2), and Photograph 1, it will be at once seen that in the claw-shaped figure, there are not many elements which can permit of precise measurement and of the comparison of one figure with another, and with those of the aluminous amphiboles. Yet the shape is so constant as to render possible an immediate recognition of these figures and of their orientation. The etch-faces are generally three in number (sometimes four, as in Plate I. Fig. 4), one plane, the others more or less curved. The drawing and photograph convey a far better idea of the arrangement of the etch-faces than could be given in a verbal description, and it will only be necessary to note a few special points. First, we have the corner at *A* (Fig. 1), which is always the most clearly defined part of the figure. Often in the initial stage of development this re-entrant angle appears before one can make out any-

thing of the rest of the figure (Plate I. Fig. 1), a phenomenon that seems to have its correlative in the filling of the deeper parts, first of the figures on a crystal of alum when it is placed in a concentrated solution of its own substance (Ausheilen).* The edge AB is likewise the most sharply outlined edge. The angle BAH which it makes with the trace of the cleavage can be seen to alter as the figure gradually evolves in the process of etching. Thus, on Zillerthal actinolite, this angle increases as the figure grows more mature, from minus 2° to plus 10° , plus angles being read on the right of the cleavage trace passing through A (compare in Plate I. Fig. 1, Fig. 2, and Fig. 3). The limits of variation are the same for the Syra actinolite. In the actinolite numbered V. 14, they are 0° and 12° ; in V. 16, 0° and 8° . During this process of swivelling, the edge AB remains straight; this suggests an actual change in the indices of the figure-face adjoining AB as the pit is deepened, rather than a modification of a figure-face of constant indices by secondary solution. An analogous feature characterizes the pits on aluminous amphibole, as will be noted further on. Again, the corner at C , while not definite enough to allow of exact location as a point, can be with low powers so fixed with reference to A and the trace of the cleavage as to orient immediately the whole figure. Measurements were made of the angle CAH , within about 2° of accuracy in each case, as follows:—

| Specimen. | Angle CAH . |
|-----------------|---------------------------|
| H. 5 | 12° . |
| H. 10 | 13° – 16° . |
| V. 12 | 13° . |
| V. 14 | 10° . |
| V. 16 | 12° – 14° . |
| V. 17 | $12\frac{1}{2}^\circ$. |
| P. 19 | 13° – 15° . |
| V. 20 | 13° . |
| V. 22 | 13° . |

This angle is then seen to vary only slightly, and it has always the same sign with respect to the trace of the cleavage. We may thus state the orientation of the pit by means of its longer axis AC ;—the point of the “claw” is directed towards the positive hemipyramids. Furthermore, the asymmetry of the figure expressed in the contrast of the curved side ADC and the side AB gives the orientation at a moment’s glance.

* Cf. Klocke, Zeit. für Kryst., 1877–78, Bd. II. p. 144.

Strongly attacked Zillerthal actinolite regularly exhibits normal etch-hills on the prism, but, since they are not of immediate interest in connection with our main purposes, I shall pass them over with this mere mention.

MONOCLINIC ALUMINOUS AMPHIBOLES. ETCH-FIGURES ON (110).

As might have been expected, I have observed a considerably greater variety in the aluminous amphiboles than in the relatively few non-aluminous species that, so far, have yielded figures that can be discussed. The pits of corrosion are, however, reducible to three types, respectively characteristic of basaltic hornblende, glaucophane, and arfvedsonite, and it is by the names of these species that we shall know the types.

The Hornblende Type (110).

To use an expressive German designation, the term "hornblende" is a "Sachname," and signifies a large number of bisilicates which are as yet not dignified by more specific names because of our ignorance of their real nature. If the phenomena of etching are to have weight in the discussion of the isomorphism or the orientation of cleavage pieces of hornblendes, it is expedient to examine an extensive and representative suite of specimens from the different members of the group, and determine what are the variations in the figures of corrosion along the series. I have accordingly etched about one hundred crystals and cleavage plates from the thirty localities mentioned in the list of materials used. The result was to show that all these species will give etch-pits whose main characters are constant, but permit of the recognition of at least four sub-types. From the localities of specimens that illustrate them best, these may be called the Wolfsberg, the Kragerö, the Edenville, and the Philipstad sub-types. With the exception of the last, crystal-face (110) and cleavage (110) give invariably the same figure.

The Wolfsberg Sub-type of Corrosion Pits on (110).

The front positive prism-face on the lustrous basaltic hornblendes of Norway, Bohemia, Vesuvius, etc., uniformly give an etch-pit, scalene-triangular in shape, with the most acute angle (corner) pointing downwards and the next most obtuse angle (corner) pointing northeast (Fig. 2, Plate I. Figs. 5, 6, 7, and 8). In a mature figure (Fig. 2), the three figure-

faces and the edges are curved, AC more than AD and DC more than AC . AB is a part of AC which is practically straight, but of variable length when compared to the pit as a whole. A, B, C , and D being the principal angular points of the figure on the outside, i. e. marking the more or less clearly defined corners formed by the meeting of pairs of figure-faces and the prism-face etched, A', B' , and D' are corresponding corners at the bottom of the pit. Their position changes with the maturing of the figure, but they are always analogous to A, B , and D , because the bottom figure-face remains parallel to (110). To get some idea of the relative dimensions of the pits we shall define the "length" of a figure as the distance, AH , from A to the foot of the perpendicular running from C to the trace of the cleavage passing through A . The "breadth" is, in like manner, the distance from this trace to the line tangent to the curved side DC and parallel to the cleavage AH . The maximum length observed was about one tenth of a millimeter and the breadth never far from one third of the length. The angle $D'A'B'$ gives an indication of the bluntness of the figure, and is selected for measurement rather than DAB on account of its greater sharpness, and hence the greater accuracy in measurement. It is strikingly constant at from 72° to 73° . The angle CAH is of course variable with the elongation of the figure, but preserves a north by east trend in all cases. Its value is usually from 13° to 15° .

The angle BAH also helps to orient the figure, and displays an interesting relation to the deepening of the pit. The shallow initial pits of V. 46 characteristically had a large value for this angle ($= 5^\circ$); as they matured, it passed through intermediate values until parallelism of AB with the trace of the cleavage was reached; there the swivelling of AB seems to have been arrested in even much older figures, and thus the angle BAH never was observed to change its sign. A cause for this swinging of AB is problematical, but it looks as if Becke's* principle of differential solution might be used in explanation. In the corner A , there is likely to be more rapid saturation with the products of solution than along the medial part of the figure-face AC , since these are not so readily whisked away in convection currents acting on the constricted parts of the pit as in those affecting the more open region about the point B , for example. Thus, the middle part of AC will suffer in a unit of time the attack of a greater number of chemically active ions than will the corners, and yield faster to solution accordingly. Such

* Min. und petrog. Mittheil., 1885, Bd. VII. p. 240.

a hypothecated process of "secondary solution" was incidentally referred to in connection with the actinolite figures; its effects can often be seen where straight-edged outlines of a figure are replaced by curved edges as the figure is undergoing destruction by prolonged solution.

Plate I. Fig. 7 furnishes a noteworthy variation on the normal and simple process of pit development. The figure is compound, and consists of three pits, formed respectively at the bottom of the next oldest pit. Each must represent an abrupt stage in the solution of this part of the surface. The side AD remains sensibly parallel to itself in all three steps, but the angle BAH grows larger from the first to the third numbered downwards; at the same time, the edges of the successive figure-faces against (110) are seen to curve more in the first than in the second, and in the second than in the third. These facts accord with those observed in the case of the pits that grew continuously, not intermittently, to maturity from the initial and less advanced stages of previous exposures to the acid. The stepped figure seems, then, to show that the formation of pits may (though not always) take place spasmodically, so to speak ("sprungweise," in the German phrasing), the attack the affair of a moment and preceded and followed by longer periods of almost perfect quiescence as regards other than "secondary" solution. Klocke believed, similarly, that the formation of figures on the alums is an instantaneous thing.* The stepped form is presumably not due to a zonal structure in the hornblende, because such a hypothesis would imply very considerable variations in the attackability in passing from the exterior to the inner zones of the crystal, — variations improbable

* Zeit. für Kryst., 1877-78, Bd. II. p. 131. The rapidity of the reverse process, that of healing over an etched surface, was early commented upon by Sir David Brewster in connection with his studies on the instructive group of crystalline substances, the alums, especially with reference to his now familiar "light-figures." On immersing an etched crystal of an alum in a concentrated solution of its own substance, he observed that, "in an instant," the pits of corrosion began to fill. He says, "The singular fact in this experiment is the inconceivable rapidity with which the particles in the solution fly into their proper places upon the disintegrated surface and become a permanent portion of the solid crystal." Phil. Mag., 1853, Vol. V. p. 27. The intermittent character of the process of etching was noticed by Rinne (Neues Jahrbuch, 1885, Bd. II. p. 15), who etched milarite with dilute HF. At first, the base became covered with regular hexagonal pits placed symmetrically on (0001). On further attack, these are *suddenly* modified by the appearance in each case of a second hexagon in the bottom of the first, but now turned through an angle of 30° .

and not yet shown to exist. The interrupted phases of solution are more reasonably connected with the lamellation of the cleavage parallel to the plane attacked. Actual microscopic or submicroscopic separation of layers parallel to this cleavage would present to the solvent action of the hydrofluoric acid a series of thin plates each of which, strongly resistant in a direction at right angles to the broad flat surface, would readily yield in directions *in* that surface, i. e. along the grain of the mineral.

The above mentioned data regarding the highly important Wolfsberg sub-type refer to conditions of etching described as standard for the present investigation. Remembering Bömer's conclusion that the temperature of the solvent has, in the case of HF and quartz, an influence on the figures, I have recorded the facts from a number of experiments intended to test the principle in its application to the group of the common and basaltic hornblendes. The experiments were made on V. 46, as follows : —

| | Temperature. | Duration of Exposure. | Result. |
|------|------------------------------|-----------------------|--|
| (1) | HF boiling on Bunsen burner. | 45 seconds. | Many poorly defined pits. |
| (2) | " " " | 90 " | Larger poorly defined pits. |
| (3) | Water bath at 100° C. | 2 minutes. | Small sharply defined pits. |
| | Standard conditions. | | |
| (4) | " " " | 2½ minutes | Pits numerous, in every case, some of great sharpness and large enough to measure. |
| (5) | " * " | 3 " | |
| (6) | " " " | 3½ " | |
| (7) | " " " | 5 " | |
| (8) | " " " | 8 " | |
| (9) | Acid slightly warmed. | 10 " | Pits indistinguishable from the last, but associated with etch-hills. |
| (10) | " " " | 20 " | |
| (11) | Room temperature | 16 hours | Few but good figures of the foregoing type. |

Throughout the whole series there is such a close correspondence in the forms and measurements of the figures that we must posit for the latter an independence of the temperature of the hydrofluoric acid, so far as any *sensible* differences are concerned.

Neither temperature nor concentration of acid, nor, indeed, any cause known to me will explain a notable variation in the shape of the pits on (110) of the amphiboles now under consideration. It consists in the appearance of an adventitious fourth figure-face on the southeast side, in addition to the three usual ones (see Plate I. Fig. 8). There is no

discoverable rule governing its development, and I even doubt that it is always the *same* face. We might suppose that BC is composed of a large number of minute planes, and that, for some at present unknown reason, there is a selection of now one, now another, of these multitudinous facets, which grows rapidly and becomes prominent as a fourth figure-face of the pit.

Pargasite, carinthine, gamsigradite, syntagmatite, and barkevikite (see Plate I. Fig. 20), each from its classic locality, give figures that are equivalent with those just described for basaltic hornblende. The differences, if any, from the Wolfsberg sub-type are so slight as to prevent any determination of these varieties from the shapes of their respective corrosion pits. The other three sub-types merit a few remarks, inasmuch as they undoubtedly owe their distinctive characters primarily to chemical composition.

The Kragerö Sub-type, (110).

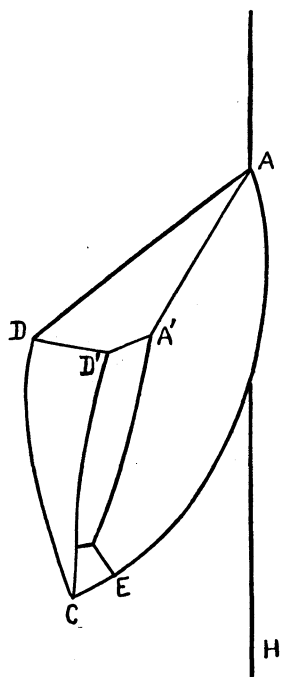


FIGURE 3.

The pits on (110) of V. 31 were somewhat sharper than those usually obtainable on basaltic hornblende (Figure 3, Plate I. Figs. 9 and 10, and Photograph 2). There are again normally three, abnormally four, figure-faces all oriented in the *sense* of the corresponding faces of the pits of the Wolfsberg sub-type. The straightness of the edge AD is here characteristic. The angle DAH is extraordinarily variable, having the value of about 38° in the initial figures, and intermediate values up to 80° in the large matured pits. There is also a swivelling of the edge $A'D'$, but its amount is difficult to determine. Accompanying these changes in the figure-faces, there is a tendency for the figure to broaden out as it deepens; so that, while in the initial figures the ratio of length to breadth is about 3.5 : 1 (0.05 mm. : 0.014 mm.), that ratio is 2 : 1 (0.072 mm. : 0.036 mm.) in the matured pit. The angle CAH ranges through limits about equal to the Wolfsberg readings.

The Kragerö sub-type differs, then, from the Wolfsberg sub-type in the lack of curvature in the figure-face $ADD'A'$, in the acuteness of the northeast angle at A , in the greater variation of shape as the figure grows older, and in the stoutness of the figure in plan. The orientation is the same in both, as also the occurrence of the adventitious fourth figure-face adjoining CE in the figure (see Plate I. Fig. 10). V. 42 is the only other amphibole that showed closely similar etching phenomena (Plate I. Figs. 11 and 12, and Photograph 3), but their clearness has led to the conclusion that we have here a new category of figures whose explanation should be looked for in the internal structure of the varieties in question. The lack of analyses forbids the extension of this hypothesis.

The Edenville Sub-type, (110).

Edenite gave abundant figures, apparently identical with those on the Wolfsberg hornblende, but the habit of a cleavage piece of the former was peculiar in exhibiting a general predominance of the four-sided figures already noted in connection with the previous two sub-types (Plate I. Figs. 13 and 14). The triangular figures do occur, but their number is quite subordinate. Even without their aid, it is very easy to orient cleavage plates of the mineral by means of fairly well developed quadrilateral figures; in them, the upper end is always recognizable.

The Philipstad Sub-type, (110).

The last of the hornblende sub-types which we have to notice is of special interest, since it led at once to further investigation and the discovery of a new and interesting variety of amphibole. Figures were produced on four different crystals, with exposures of 2 min., 2 min., $1\frac{1}{4}$ min., and 2 min., respectively, and on another crystal immersed in hot HF (near its boiling point) for one minute. In all five, the result was the same, two clearly defined figures, whose distribution was at first a mystery; on further study it was found that one type was confined to the cleavage faces and the other to the crystal faces, or to cleavage surfaces lying not more than 1 mm. beneath the latter. We begin with a description of the first mentioned sort of figures.

They vary in number of sides, in tint (proportion and distribution of light and shade), and considerably in shape (Photographs 6 and 7). Usually, they are six- or seven-sided and bounded by nearly or quite straight edges (Photograph 6), and either uniformly dark or more or less brilliantly illuminated on certain figure-faces. I could get no satisfactory

idea as to the relative steepness of the figure-faces on account of the great variability of the pits, on the one hand, and, on the other, the deep tint characteristic of the pits. The largest mature pits are perfectly black, blunt on the upper end because of the truncation by a long transverse edge and bulging below but tapering rapidly to the lower end. The angle made by the transverse edge with the cleavage trace was measured at 83° , a value which lies within the limiting values of the angle DAH , in Figure 2; the edge is thus oriented the same as the edge DA of the Wolfsberg sub-type, and the two are regarded as equivalent.

Now, these pits appear on all four cleavage faces and are also associated on these according to the law of twinning after (100); but with them were found a second set of pits arranged enantiomorphously to the first. Evidently, no system of twinning can explain their orientation, and it is all the more surprising from the fact that there is no perceptible difference in the young forms of the two sets of figures. Moreover, whole areas of a cleavage surface are covered with pits belonging to a third category, in which the straight edges are the exception and a curved outline the rule (Photograph 7). By an optical illusion, these pits have the appearance of projecting from the general surface after the manner of etch-hills; in so doing, the form of the outline and a pronounced shelly structure, exactly imitating the lines of growth in a molluscan shell, make each pit extremely organic in look. Very often, the shells are greatly elongated in a direction transverse to the cleavage trace (Photograph 7). Only one probable explanation of these two classes of abnormal pits has suggested itself, namely, that the crystals are in a condition of internal tension, which interferes with the workings of the usual molecular cohesions. If this hypothesis be correct, we should expect all transitions between the normal type and the other two abnormal types of figures. Such is the fact, typified in the observed occurrence of pits intermediate to those of the first and second kinds, where the transverse edge is seen to have all directions within the limits set by the enantiomorphous pits (see Photograph 6). Moreover, we might expect on this hypothesis that there should be distorted pits on the cleavages etched with reagents other than HF. Using caustic soda, I obtained normal pits on (110) illustrated in Photograph 9; occasionally, though more rarely than in the case of crystals etched with the acid, the beautifully marked shells were replaced by others elongated transversely.

A possible cause of this distortion by differential tensions is not far to seek. Several carefully cut sections of the mineral showed that it is strikingly zoned, each zone possessing its own tint of color which is

doubtless correlated with a special chemical constitution. It is not difficult to believe that the molecular substance of the crystals may be put into a condition of strain by varying rates of expansion and contraction in the different zones due to temperature changes. Again, there is also possible a massive stress set up in the crystal caused by its contortion in the rock from which it was derived. In this case, we are dealing with a druse-mineral; nevertheless, I have observed that at least two of the individuals are greatly twisted so that the plane of the cleavage is replaced by a curved surface with from 8° to 10° of curvature. Attempts were made to etch this particular crystal on (110), without marked success, although the mineral was strongly attacked; yet the few pits actually obtained seemed to be of the distorted types. May this massive distortion not be the result of differential stress in the zones? *

The Philipstad (cleavage) sub-type of etch-pit is thus analogous to the other sub-types peculiar to hornblendes, but it is *similar* to no one of them. It bears the same relation to the second principal kind of pit observable on this mineral; namely, that on the zone occurring on all the individuals so far examined, just underlying the crystal face (Photographs 4 and 5). Most commonly, they are of the shape illustrated in Photograph 4; that is, while the general habit of the figure is very like that of the Wolfsberg sub-type, there is here a more pronounced blunting of the lower end of the pit by an edge nearly as long as the transverse edge of the upper end. The rarer pits with a sharpened lower end are portrayed in Photograph 5. The photographs show with sufficient clearness the contrast existing between these pits and those characteristic of the inner zones exposed on cleavages. There is never any intermixture of the two kinds; the former is confined to a light colored exterior zone, which appears to be less strongly charged with iron than the inner zones, which are always darker in color. Examination proved that these pits on the outside zone could not be explained as *natural* etchings; they are manifestly the result of an interaction between the acid and the mineral, and probably differing from the figures on the other zones on account of the fact that, while the latter agree in chemical composition fairly closely among themselves, there is a strong chemical peculiarity adhering to the outer zone. That the phenomenon is not confined to the reagent used is evident from the comparative study of

* *Sudden* twisting of crystals does not seem to affect the form of the etch-figures. Thus, I etched a cleavage plate of gypsum which had been bent through an angle of at least 15° . The pits produced had perfectly normal characters, as those recently described by Viola.

Photographs 8 and 9. No. 8 indicates the result of etching (110) (crystal face) with caustic soda. The pits are like those on the inner zones in possessing a shelly structure, but have a different outline (compare Photograph 9).

Before leaving this peculiar hornblende, it should be stated that it stands also in a unique position with respect to the etching properties of the clinopinacoid. I have called the angle ADH in Figure 8 positive; it varies in value with the different varieties of aluminous amphiboles from 1° to 10° . But, in the analogous pit produced on (010) of the Philipstad hornblende, this angle is always *negative* and averages $2\frac{1}{2}^\circ$ in value. The description of the optical and other characters of the mineral is deferred to another occasion. (See following article.)

Etch-Hills on Hornblende, (110).

A digression from the main subject of types of pits of corrosion may be permitted in the form of a short discussion of another result of attack with hydrofluoric acid, namely, etch-hills. The usual effect of dissolving a cleavage piece is, in time, the disappearance of the pits formed at the beginning, and their replacement by these residual bosses. When they are numerous, the mineral has a characteristic mammillated look. Besides the normal bosses left on the removal of the ridges between successive pits, however, there often appear on aluminous amphiboles, when etched rapidly (fresh acid and high temperature), a variable number of remarkable etch-hills which, from their form, can have but little to do with those just mentioned.

As examples, V. 46 furnishes some very striking specimens. I produced these peculiar etch-hills at 3 minutes, at $3\frac{1}{2}$ minutes, at 7 minutes, and also after 12 minutes' suspension in HF gas evolved from a hot (fuming) aqueous solution of that gas. In all four cases, the bosses were on the whole similar in look, and, on account of their perfect development, I shall describe the etch-hills on the cleavage piece last mentioned, as typical of all (Photograph 10). They are bizarre in form and arrangement; in plan, triangles, irregular quadrilaterals of many shapes, trapezoids, pentagons, etc., sometimes in groups of two, three, or a half-dozen, similar to one another in outline, and even showing parallelism between corresponding sides. They are commonly bounded by straight lines that have no definite relation to the hornblende crystal, and are thus in striking contrast to the pits which are oriented in the regular way on the same cleavage face. Occasionally, small groups of the figures have the same form and orientation; thus, three scalene triangles were observed

in one place, with sides mutually parallel. At the same time, other aggregations could be found in which the individuals were bounded by the same number of sides, and with angles sensibly equal, yet the corresponding sides were not parallel and the orientation of the figures was necessarily unlike.

For some time I was without a clue to the meaning of these myriad extraordinary figures, but another of the many valuable suggestions in Becke's writings afforded some light on the problem.* When galenite is etched with hydrochloric acid, the resulting chloride of lead often crystallizes out in areas of local supersaturation of the liquid, particularly in regions where the pits are most numerous. The individual crystals of the chloride may be locally oriented in the same way, and will doubtless, in certain cases, favor a skeleton growth. They serve as a kind of protection to the surface on which they lie; the acid will thus dissolve the intervening parts of the general crystal-surface not so protected, and the substance of the galenite underneath the chloride crystals is left projecting as residual hills on corrosion. The common orientation of these crystals and their skeleton-crystallization (touching the galenite surface only where the regular growth of skeleton crystals would permit) could explain the accordant attitude of certain similarly arranged groups of the bosses.

An analogous explanation is believed to apply to the curious etch-hills on hornblende above noted. The chemical reaction is different, the mechanical cause of differential attack is the same. Instead of hydrochloric acid we have here hydrofluoric acid, and in place of a single resulting compound, the chloride, there are probably several salts of hydrofluoric and fluosilicic acids that are produced during chemical solution of the bisilicate, and in the form of crystals or of skeletal aggregates might serve as the protective caps in the lithographic process. What particular fluorides and silicofluorides would be most likely to play such a role, it is perhaps not impossible to say. From their relative insolubility in warm water, the prisms of fluosilicate of magnesium, the rhombohedrons of the fluosilicate of iron, and the spindle-like crystals of the fluosilicate of calcium, seem to be the most favorable to such action. The more soluble octahedrons of the fluosilicate of sodium and hexagonal prisms of the fluosilicate of potassium might also result in an atmosphere of hydrofluoric acid gas diluted with only a small proportion of vapor of water,

* Aetzversuche am Bleiglanz, Min. und petrog. Mittheil., 1884-85, Bd. VI. p. 240.

as in the case before us. The tendency of fluosilicate of magnesium to crystallize out in the form of skeletal groupings is noted and figured by Bořický in his classic work on microchemical methods.* He also describes the actual determination of these various fluosilicates on (010) of an amphibole,† etched with hydrofluosilicic acid.

The Glaucophane Type, (110).

Glaucophane furnishes a new type of pit on (110). It is more elongated than the Hornblende type, is characterized by a more pronounced straightness of edges, and is unique by reason of the parallelism between its longest edge (corresponding to $A\ C$ in Figure 2), and the trace of the cleavage. (See Plate I. Figs. 15 and 16.) It is likewise triangular in outline, possesses three figure-faces on the sides and a migrating bottom face. Gastaldite from the Champ de Praz (P. 59) afforded pits in no respect to be distinguished from those on the Ile de Groix glaucophane. On the other hand, crossite gave figures decidedly differently and more closely allied to the Hornblende type (Plate I. Fig. 17).

The Riebeckite Type, (110).

Figures of corrosion were obtained on riebeckite only with much difficulty, apparently due to its extreme attackability in concentrated acid. They were always excessively small, often with imperfect development; the upper end of the pit was the first to become clearly evident, in the process of maturing. The figure has many points in common with the sub-type noted above on Edenite; it is usually quadrilateral, though sometimes three-sided and analogous to the Wolfsberg sub-type. But it differs from both in its being much *darker* than they in vertically incident light: — the figure-faces are steeper than in the same (110) pit on common hornblendes (Plate I. Figs. 18 and 19).

The Arfvedsonite Type, (110).

Quite an exceptional category of etch-figures is represented in the pits generated on the prism-face of arfvedsonite by the use of hydrofluoric acid. (Plate I. Figs. 21 and 22, and Photograph 11.) Their peculiarities are so salient as to enforce the belief that, in the matter of cohesion on this particular face, arfvedsonite is at least as far removed from the

* Archiv d. naturw. Landesforschung von Böhmen, III. 5, Prague, 1877, Plate I. Fig. 12. Translated by Winchell, 19th Ann. Rep. Minnesota Geological Survey.

† *Op. cit.*, Plate II. Fig. 7.

other amphiboles as it has been proved to be optically. The pit is here a spindle-shaped well defined figure, generally about six times, rarely only four times, as long as it is broad. The spindle is usually ideally perfect, and then the axis can be seen to make an angle with the cleavage cracks of two degrees east of north on (110), two degrees west of north on ($\bar{1}\bar{1}0$). Many pits show that they are bounded by two curved figure-faces of unequal steepness, and hence of unequal illumination in the microscope. The narrower, darker one lies to the left on (110); it is separated from the other by a narrow light streak that corresponds to the keel of the unsymmetrical canoe. The relations are enantiomorphous on ($\bar{1}\bar{1}0$). Occasionally, the spindle is blunted with what appears to be an imperfectly formed third figure-face that would represent the upper figure-face of the Hornblende type (Plate I. Fig. 22). The photograph does not give an idea of the exceeding sharpness of these figures, at least as compared with most other amphiboles; there can be no doubt that the type is a distinct one and stands alone.

The figures show the mineral to be holohedral and centrosymmetric and a cleavage plate can be easily oriented in the absence of crystallographic data by observing the position of the adventitious third face, or the direction of the spindle-axes with respect to the obtuse angle of cleavage (110 : 110), and one, say the darker, of the two longitudinal figure-faces of a pit.

Both the symmetry and orientation of arfvedsonite are, however, better made out by the use of figures resulting from exposure to molten caustic soda. A cleavage piece was found after 25 seconds' immersion to be covered with three-sided pits, as depicted in Figure 4. These show once again the radical difference in behavior between arfvedsonite and common hornblende. (Cf. Plate I. Figs. 34 and 35.) It is, furthermore, an interesting case, in that the directions of rapid solution are here transverse to those of rapid solution by the acid, and, secondly, the formation of etch-figures is once again seen to be independent of cleavage.

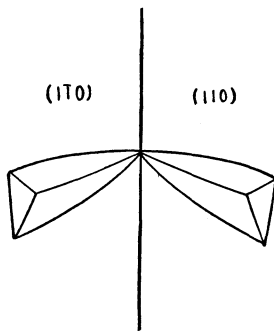


FIGURE 4.

NON-ALUMINOUS AMPHIBOLES, ETCH-FIGURES ON (010).

The actinolite of Zillerthal was found to be typical of the whole group of amphiboles not containing a sesquioxide as regards the facts

of etching on the clinopinacoid. Good figures are obtained with ease. (Plate I. Figs. 23*a*, 23*b*, 23*c*.) They are remarkable in belonging to two classes, analogous to those described by Pelikan for pyroxene with the same reagent.* (Photo. 12, cf. Photo. 13.) The pit of the one category is a quadrilateral in outline, with four pyramidal figure-faces and a bottom-face that grows smaller and then disappears as the figure matures and deepens. The other kind of pit is also four-sided in habit, but may possess another pair of figure-faces in addition to the five corresponding to those of the first class. Figures 5*a* and 5*b* represent diagrammatically the two kinds matured under normal conditions (water bath, concentrated acid, etc.). The drawings are lettered in order to indicate the elements chosen to fix the shape and orientation of the pits.

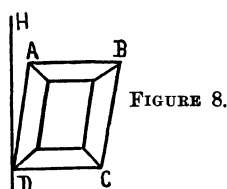


FIGURE 8.

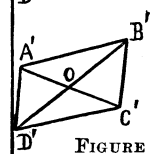
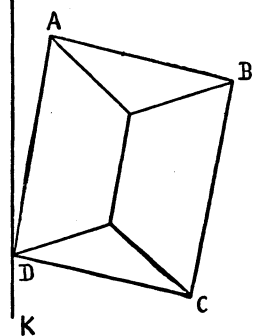
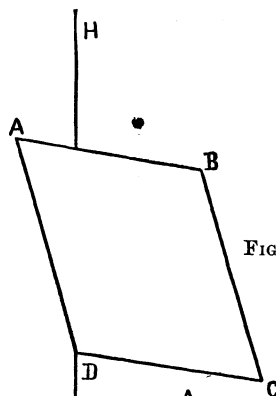
FIGURE 5*a*.FIGURE 5*b*.

FIGURE 6.

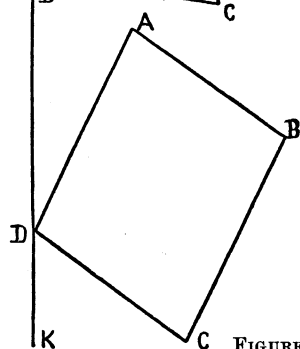


FIGURE 7.

* Ueber den Schichtenbau der Krystalle. *Min. und petrog. Mittheil.*, 1896, Bd. XVI. p. 16.

The smaller pits (Figure 5 *a*) are invariably four-sided and elongated parallel to the side the more oblique to the trace of the cleavage. So extremely minute as to be at times easily overlooked, they are, moreover, inconspicuous on account of their shallowness and the consequent lack of contrast with the rest of the crystal surface; they may hence be called the "light" figures to distinguish them from their darker fellows of the second class to be described. The angle $A'D'H$ was determined at from 3° to 5° , the angle $B'A'D'$ averaged 108° . $A'B'$ and $A'D'$ were measured as under:—

| $A'B'$ | $A'D'$ | Ratio, $A'B' : A'D'$ |
|-----------|-----------|----------------------|
| 0.012 mm. | 0.012 mm. | 3 : 3. |
| 0.011 " | 0.009 " | 11 : 9. |
| 0.014 " | 0.012 " | 7 : 6. |
| 0.014 " | 0.010 " | 7 : 5. |

On the average, $A'B' : A'D'$ is about equal to 8 : 5.

Quite different are the pits of the other kind (Figure 5 *b*); they are larger, deeper, and often more numerous. The elongation is, in this case, in the sense of the vertical axis of the crystal. The four-sided figures are, as in the first class, parallelograms in plan, the acute angle here lying, however, in the upper *left* hand corner. It is this corner and the opposite one that are truncated by the accessory pair of figure-faces already mentioned. The angle ADH is 8° instead of 3° – 5° in the light figures. The angle BAD varies from 82° to 88° ; the curvature of the sides prevents a close determination. The limits of variation in the ratio $AB : AD$ were observed as 1 : 1 (0.04 mm. : 0.04 mm.) and about 2 : 3 (0.032 mm. : 0.048 mm.).

According to the character of the figure-faces (always pyramids) these larger pits can be subdivided into two sub-groups in one of which the faces AB and CD are equally illuminated but darker, i. e. more steeply inclined to (010) than AD and BC , also of equal brightness, while in the other group the reverse relation holds. (The figure-faces are here indicated by their corresponding edges of intersection with (010).) Both kinds have figure-faces belonging to the same crystallographic zones, and they are probably allied as are the figure-faces described by Baumhauer on apatite.* He noted — that which is evident from his photographs — that, as the apatite matures (deepens) its faces become steeper and steeper on (0001), ("Verschleppung" of Becke). In one case, I discovered a large pit having AD steeper than AB , with the bottom occupied by a

* Resultate der Aetzmethode, p. 48.

second typical pit manifestly of younger generation, but with its AB steeper than AD . Brauns found on the etched surface of sylvite neighboring pits bounded by figure-faces of different steepness, but he does not seem to have connected the phenomenon with the difference of maturity of the two pits. (See Neues Jahrbuch für Min., etc., 1889, Bd. I. p. 113.)

Either of these types of dark figures may show a keel at the intersection of a pair of figure-faces (Plate I. Fig. 23 *b*).

It was in connection with the study of the pits on (010) of actinolite that I became convinced of the necessity of fixing a standard degree of dilution of the hydrofluoric acid before beginning a series of comparative experiments in etching the amphiboles. The problem could be here more successfully attacked than in the examination of the figures on (110) because of the greater likelihood of being able to observe differences in the shape or arrangement of the systematically straight-edged pits on (010). Six cleavage pieces of Zillerthal actinolite were immersed in HF, either in the form of pure gas or in different states of dilution with water. The procedure and the results are synopsized in the accompanying table, which shows the effects on the angles ADH and BAD of the dark figures under the different conditions (Figure 6).*

| Specimen. No. | Solvent. | Exposure. Minutes. | Angle ADH . | Angle BAD . |
|------------------|---------------------------------|-----------------------|---------------|------------------|
| (1) | Pure HF (gas) | 70 | 13-14 | 76 |
| (2) | Com. conc. water solution of HF | 2½ | 12 | 75 |
| (3) | 75% HF, 25% water | 4 | 2 | 64 |
| (4) | 50% HF, 50% water | 15 | -2 | Acute but indet. |
| (5) | 25% HF, 75% water | 25 | -11 | " " |
| (6) | 10% HF, 90% water | 20 | -16 | " " |

No. 1 was etched by hanging it above the surface of some concentrated water solution of the acid, that was very gently heated far below its boiling point, and thus only a small percentage of water vapor could be present during the reaction. The other examples were etched in the ordinary way on a water bath. The percentages of dilution are by volume.

The effect of dilution with water is, then, to produce a rotation of each dark figure about a line perpendicular to the crystal plane. The direction of the rotation is opposite to that of the hands of a watch, its amount (within the limits of these experiments) about 30°. Along

* For Figures 6 and 7 see page 406.

with the rotation, there is a simultaneous distortion of the outline so as to make the angle BAD more and more acute. The latter could not be measured closely in the cases of dilution of 50 per cent or more on account of the poor development of the pits. The longer edge preserved its distinctness much better than did the shorter edge; hence the angle ADH was measurable throughout.

The light figures remained quiescent, neither changing in shape nor orientation, so far as those rather unsatisfactory figures would permit of measurement. In the same manner, I could discover no variations in the pits on the prism-face (110).

Bömer has described other examples of the dependence of the results of etching with hydrofluoric acid on its state of dilution in water. He found the form and attitude of the pits on the base of quartz to alter so much with dilution that, whereas concentrated acid gives figure-faces belonging to the right trigonal pyramids, with very dilute acid they are negative rhombohedrons. Intermediate forms characterize degrees of concentration between these two extremes.* Baumbauer discussed a similar anomalous behavior in the pits on apatite, using hydrochloric acid as the solvent.† There is throughout a close analogy between the pits on (0001) of apatite and those on (010) of actinolite. In both, we have dark figures and two categories of light figures, and, finally, the same tendency to rotate with decreasing concentration of the respective acids in aqueous solution.‡

It is well known that sulphuric acid, when added in small quantities, will in certain cases intensify the solvent power of hydrofluoric acid. I made one or two trials of a basaltic hornblende to see whether in this way the figures of corrosion might be improved. They resulted in partial failure, for, although the pits were a little larger than usual, they lost considerably in definiteness of outline. It then occurred to me to try mixtures of the two acids in various strengths on a more resistant substance, actinolite, primarily to determine what, if any, would be the influence of the sulphuric acid on the etching. The problem was analogous to that just discussed for dilution with water, the procedure was similar, the results just as striking. The table is so like the last as to need no special explanation. (Figure 7.)

* Neues Jahrbuch für Min., etc., 1891, Beil. Bd. VII. p. 535.

† Resultate der Aetzmethode, p. 48.

‡ Becke states that concentration affects the position of the figure-faces in the *etch-zone*. Min. u. petrog. Mittheil., 1883, Bd. V. p. 487.

| Specimen. No. | Solvent. | Exposure. Minutes. | Angle ADH . ° | Angle BAD . ° |
|------------------|---------------------------|-----------------------|--------------------|--------------------|
| (1) | Pure HF (gas) | 70 | 13-14 | 76 |
| (2) | Commercial conc. solution | 2½ | 12 | 75 |
| (3) | 95% HF, 5% H_2SO_4 | 5 | 11-12 | 75± |
| (4) | 90% HF, 10% H_2SO_4 | 3½ | 19 | 74-78 |
| (5) | 75% HF, 25% H_2SO_4 | 8 | 19± | 76-78 |
| (6) | 50% HF, 50% H_2SO_4 | 3½ and 8 | 23 | 79± |
| (7) | 20% HF, 80% H_2SO_4 | 3½ | 26± | Indeterminable. |

The mixtures of acids were proportioned by volume.

The table clearly expresses a rotation of the figures with increasing percentages of H_2SO_4 in a right-handed direction, that opposed to the direction of movement in the water-dilution series. At the same time, the angle BAD grows larger, and thus the parallelogram tends more and more towards a rectangular outline. In both respects, the influence of sulphuric acid is in the shaping and the arranging the pits on the clinopinacoid, when etched by means of a mixture of that acid and hydrofluoric acid, the reverse of that of pure water mixed in the same manner with hydrofluoric acid. I am not prepared to offer any explanation of this interesting phenomenon.*

It may be noted that the surface of cleavage (110) exhibits great changes in the etch-figures as the proportion of the sulphuric acid increases. With only 5% of the latter (Plate I. Fig. 24), there is a sensible variation in look from the normal type, and in the 50% solution a strong suggestion of the Wolfsberg figure of common hornblende (Plate I. Figs. 25*a* and 25*b*).

Tremolite and richterite afforded, on the clinopinacoid, etching phenomena identical with those described for actinolite when exposed to concentrated HF; the last mentioned experiments of mixture were not essayed in connection with them.

* Baumhauer not only showed a rotation of the figures on the basal plane of apatite with increasing dilution of the solvent, hydrochloric acid, but he also established a rotation in the same direction when nitric acid was substituted for the hydrochloric, and a rotation in the *opposite* direction if sulphuric acid be similarly employed. Ref. in Bömer's article, Neues Jahrbuch für Min., 1891, Beil. Bd. VII. p. 538. The accumulation of such facts as these makes it difficult to follow Becke in the hypothesis that his "Haupttaetzflächen" have simple indices, because of greater molecular density in planes having such indices. The molecular density evidently does not change with the solvent. (Min. u. petr. Mitth., 1887, Bd. VII. p. 200).

ETCH-FIGURES ON THE CLINOPINACOID OF ALUMINOUS
AMPHIBOLES.

The cohesional properties of the plane (010) on any one of the aluminous amphiboles are simpler than those of the same face on actinolite, in that we find the development of only one kind of figure on the former though etched in exactly the same fashion. It corresponds to the light type on the actinolites in several respects, being a parallelogram with the obtuse angle situated in the upper left hand corner and the non-appearance of the adventitious third pair of figure-faces. The equivalence is not complete because of the slight elongation in a vertical sense, and because of a greater obliquity of the figure-faces to the plane (010). (See Fig. 8 on page 406, and Plate I. Fig. 26, and Photograph 14.)

We have seen that the pits on (110) of the hornblendes vary somewhat with the chemical composition; the same is true of the (010) pits. A number of specimens from different localities undoubtedly with considerable, though unknown differences in the proportions of the constituent oxides, were etched, and two of the elements determined in each case, as recorded in the table: —

| Specimen. | Exposure. Minutes. | Angle ADH . | Angle BAD . |
|-----------|-----------------------|---------------|-------------------|
| V. 26 | $1\frac{1}{2}$ | 5 | 95 |
| V. 32 | $1\frac{2}{3}$ | 4 | 113 |
| V. 33 | 1 | 5 | 98± |
| V. 34 | $1\frac{1}{2}$ | 7 | 95 |
| V. 40 | 1 | 7 | 97 |
| V. 42 | 1 | 10 | 100-105 |
| V. 54 | 2 | 1 | Not determinable. |
| P. 55 | 3 | 4 | 114 |

There can be no question, in view of the facts of the foregoing table, that there is a lack of uniformity in the crystallographic zones into which the figure-faces on (010) of hornblendes fall. The differences in outline and orientation are so salient as to impress the eye at once on seeing them in the microscope. Now those hornblendes (V. 26, V. 33, V. 34, V. 40, V. 54) which had the edge AB not far from being sensibly perpendicular to the trace of the cleavage were also characterized by (110) pits of the Wolfsberg sub-type, and those so far studied (V. 32, V. 42, P. 55) that showed important variations from that orientation carried pits more allied to the Kragerö sub-type, if not identical with it. More detailed investigation in the future with carefully analyzed material

may reduce the figures and their individual characters to law, and make the etch-pits of determinative value.

Owing to lack of material, etch-figures were not obtainable on the clinopinacoid of barkevikite, crossite, glaucophane, riebeckite, or arfvedsonite.

AMPHIBOLE ETCH-FIGURES ON FACES OTHER THAN (110)
AND (010).

From the preceding sketch of the pits of corrosion on the prism and clinopinacoid of the aluminous and non-aluminous groups of amphiboles, respectively, it is evident that the general figure-types are modified by variations in the chemical nature of the species. But the prime important modifications are conditioned by the presence in the molecule of alumina, or at least of a sesquioxide. That is, in the one class, we have to do with amphiboles whose molecular constitution is similar, excepting perhaps arfvedsonite; whether it be lime, iron, magnesia, or soda, — any or all of them, — that, together with alumina, compose the complex silicate, the results of etching are always similar.* On the other hand, so soon as the alumina (sesquioxide) molecule disappears, or is present in only very small amounts, there is a radical change in the etch-pits on both faces. This leads to the expectation that other planes will show corresponding change. The few specimens which I have been able to secure confirm that conclusion, and a brief account of the observations thereupon may prove of interest.

Before proceeding directly to them, however, I shall state the negative results characterizing the examination of three other faces (130), (011), and (111); their indefinite etching phenomena did not allow of comparisons by measurement. V. 42 at one minute's exposure exhibited many pits on (130). They were warped triangles, with the upper acute corner pitching into the crystal much after the manner of the analogous hair-like projections described by Tschermak on siderite. (See Baumhauer, *Resultate der Aetzmethode*, Microgram 20.) The same crystal of V. 42

* Mr. Walker's use of the term "similar" to denote an enantiomorphous relationship between etch-figures seems to me to be inadvisable since it is not needed in that sense, and such a usage deprives us of a convenient designation for figures that are not identical but differ from one another very slightly as in the case of the hornblendes. (*American Journal of Science*, 1898, Vol. I. p. 181.) "Analogous" might be employed in this connection rather more freely to mean similarity in some one or more features, and would need supplementary statement to indicate wherein the analogy consists.

furnished arrow-headed etch-hills on (111). The direction of the arrows was in the sense of, though not parallel to, the b axis inwards. On (011), likewise, the figures of corrosion were etch-hills of triangular shape, in the case of both actinolite and hornblende, but again so ill defined that no certain statement of likeness or unlikeness could be made. V. 16 (actinolite), V. 8 (tremolite), and V. 20 (richterite), at respective exposures of two minutes, two minutes, and one minute, show strong attack on the terminal planes and the development of numerous bosses on (011); the same was true of the hornblendes, V. 33 at two minutes, V. 35 at 1 min., V. 36 at $1\frac{1}{2}$ min., and V. 42 at 1 min. Though characteristic, they do not lend themselves to analysis, and I have been able to accomplish nothing toward comparative detailed study.

Better success was had with the orthopinacoid. Among the aluminous amphiboles, crystals of V. 33, V. 34, V. 35, and V. 42 gave pits at $1\frac{1}{2}$, $1\frac{1}{2}$, 1, and 1 minutes respectively. The result was uniform, — a figure of triangular outline, isosceles, the upper apical angle bisected symmetrically by the plane of symmetry of the crystal. The figure-faces correspond to the edges; two very steep pyramids, a dome at the base and a bottom-face parallel to (100), which diminishes as the pit matures. Occasional figures on V. 42 were notable for the replacement of the pyramids by two pairs of positive and negative pyramids (Plate I. Fig. 28). A much commoner variation is the symmetrical curving of the two lateral edges, probably as an effect of secondary solution as the figure grows older. Simultaneously, the figure tends to grow stouter; thus, a young, light figure of V. 33 was found to have a ratio of altitude to base of 4 : 1, while on the same face a dark matured figure possessed a ratio of 3 : 1. The stoutest figures measured on any hornblende (V. 34), showed a ratio of 3 : 2.

Actinolite pits on (100) display one noticeable difference, and only one, from these last figures; they are more slender (Plate I. Fig. 27). The ratio of altitude to base in the pits of V. 17 (at CA $2\frac{1}{2}$ min.) changes from a value of 6 : 1 in the initial figure to a minimum of 3 : 1 in a matured pit. Whether this distinction applies to all the non-aluminous amphiboles or not is a question that needs for its solving more material than I have had the opportunity of studying.

Finally, we have to note the corrosion pits on the dome (101).

These are, on the whole, rather difficult to obtain on hornblende by reason of the narrow limits between maximum and minimum times of exposure necessary to bring about their maturing properly. Only three of the species examined afforded good figures, and only one gave those

capable of fairly accurate measurement. The crystals belonged to H. 30, V. 35, and V. 54. The first yielded figures after 30 seconds' boiling in conc. HF, the second on one minute's exposure on the water bath, and the third after two minutes' immersion in a dilute (10%) solution of HF. The plane (101) was in every case strongly affected, and pentagonal pits of corrosion were visible (Fig. 9, and Plate I. Fig. 30).

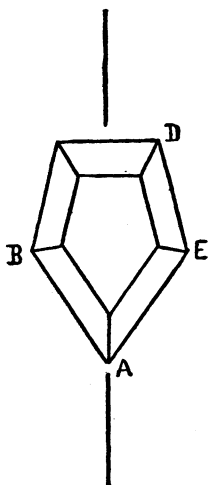


FIGURE 9.

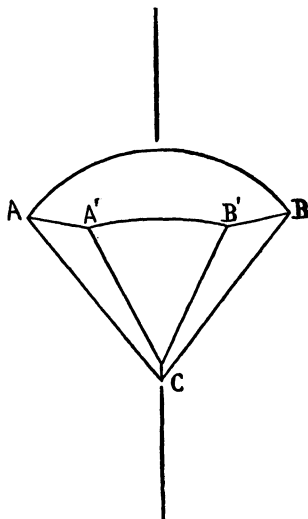


FIGURE 10.

The measurements on the crystal of V. 35 were as follows: —

$$\angle BAE \ 84^\circ. \quad \angle BCD \ 96^\circ. \quad \angle ABC \ 132^\circ.$$

The outline is symmetrical to the plane of symmetry of the crystal. The acute angle BAE points toward the front (in Tschermak's orientation). Each edge corresponds to a plane figure-face indicated in the drawing, and there is a diminishing bottom-face parallel to (101). The twinned character of V. 54 was clearly manifested in the attitude of the pits on the two adjacent dome-faces intersecting in the twinning-plane (100).

An actinolite (V. 16 at two minutes' exposure) and richterite (V. 20 at one minute) furnished the type of (101) pits characteristic of the non-aluminous amphiboles (Plate I. Fig. 31, and Fig. 10). The figures on the former were extremely sharp, but a photograph could not be pre-

pared on account of the roughness of the general crystal-surface. They are not pentagonal but triangular; two edges, $A' C$ and $B' C$ (Fig. 10), meet at an angle of 80° or more, the apex of which points forward on the crystal. The edges $A' C$ and $B' C$ are quite straight, and their respective figure-faces are plane. On the other hand, the figure-face $A B B' A'$ is curved and is predominant as a curve even when $A' C$ and $B' C$ are not well developed. The bottom plane of the pit is a plane parallel to (101) and diminishing in size as the pit matures. $A' C$ and $B' C$ are steeper (darker) than $A B B' A'$, but are of equal obliquity to (101), thus agreeing with the other characteristics of the pit in supplying perfect monosymmetry for the figure with respect to (010).

The differences in the etch-pits on the positive unit-dome of the actinolitic species as contrasted with the corresponding pits on hornblendes is striking in face of the fact that we have already seen exemplification of even greater contrasts between the mineral groups in the behavior of the unit prism and the clinopinacoid during the same process of etching.

ISOMORPHISM IN THE AMPHIBOLES.

Chemical crystallographers are of different opinion regarding the value of etch-figures in determining isomorphism. Arzruni, on the one hand, denies any necessary relationship between them and the fact of isomorphic mixture; * in this he is supported by Baumhauer, who regards the pits on dolomite, calcite, and siderite as not indicating lack of isomorphism, although their orientation on corresponding faces of all three species is widely different.† The opposite view has been strongly maintained by Retgers in his recent and valuable research on the subject.‡ Retgers gives his three criteria of isomorphism as follows: — 1. Mixtures of the constituent salts of an isomorphic series must take place in all proportions. 2. There must be a lack of chemical combination in the mixture: thus diopside (CaMgSiO_3) is not a member of the isomorphic series (CaSiO_3 and MgSiO_3), but an independent body. Likewise manganese augite (MnSiO_3) and the manganolime augite (MnCaSiO_3) are not isomorphic. 3. Etch-figures produced on the same crystallographic plane of all members of the series will be alike both in shape and symmetry. To support the last statement, he cites a

* Phys. Chemie der Krystalle, 1893, p. 162 *et seq.*

† Resultate der Aetzmethode, p. 37.

‡ Beiträge zur Kenntniss der Isomorphismus. Zeit. für phys. Chemie, 1895, Bd. XVI. p. 36.

number of such isomorphic groups whose etch-figures are known, and in every case there is this similarity among the figures. Thus the experiments of Baumhauer on the double sulphates,* the lime and strontium hyposulphates,† the alums,‡ the phosphate (arsenate) group,§ and the apatite family;|| the studies of Baumhauer and Becke on the carbonates of iron and magnesium;¶ those of Wulff on the barium, strontium, and lead nitrates,** and Becke's on spinel and its relatives; †† all exhibit a marked stability in the form of the etch-pits as the different members of each group are attacked by the same reagent. The earlier objections of Arzruni are considered to have been met by more recent observations of Baumhauer (*Res. der Aetzmethode*, p. 40). Retgers does not contend that similarity of etch-figures implies isomorphism, as in the two cases of calcite and soda nitrate on the one hand, and the rutile-zircon-cassiterite group, on the other; but regards the converse as a fixed law, "das erhärtete Gesetz," that genuinely isomorphic substances always show, on corresponding surfaces, similar etching phenomena. He further states that "a successful study of isomorphism, without continual controls by means of the methods of etching, is no longer conceivable." ‡‡ At the same time, he remarks that the etch-figures do vary, and that the limits of variation in most groups have not yet been determined; they are, however, as far as known, always narrow limits.

Now, if this contention be valid, the application of the principle to the amphiboles will have important consequences. It will be remembered that tremolite, actinolite, richterite, and astochite, from many different localities and of various chemical composition, gave uniformly the same etch-pits on (110), and, where the material was at hand to determine the point, the same figures on (010), (100), and (101). With respect to the same planes, the much greater group of common and basaltic hornblendes, also of very variable composition, agreed among themselves as well as with barkevikite, glaucophane, crossite, and riebeckite; but each of these two sets of etch-figure types was so strikingly different

* *Resultate der Aetzmethode*, p. 46.

† *Zeit. für Krystallographie*, 1877, Bd. I. p. 54.

‡ *Ber. der k. bayr. Akad. d. Wissenschaften*, 1874, and *Res. der Aetzmethode*, p. 45.

§ *Resultate der Aetzmethode*, p. 43.

|| *Ibid.*, p. 39, and earlier references therein.

¶ *Ibid.*, p. 67.

** *Zeit. für Kryst.*, 1883, Bd. IV. p. 142.

†† *Min. und petr. Mitth.*, 1885, Bd. VII. p. 200.

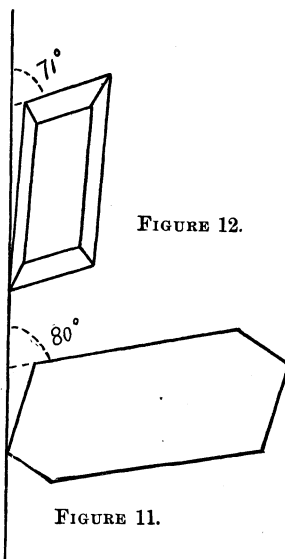
‡‡ *Zeit. für phys. Chemie*, 1896, Bd. XX. p. 528.

from the other, that, on etching (110), (010), or (101), one could tell with ease whether he be dealing with an amphibole of the first class, devoid of a sesquioxide, or with one of the second, probably aluminous, but possibly one whose iron represented the total content of sesquioxide. The testimony of the etch-pits, then, would be to establish perfect isomorphism in each of the two groups, but to refute the idea that there is isomorphism between the two groups themselves. Whether or not this hypothesis be justified by future investigation, the facts of the case seem to have an important bearing on the theory of Retgers.

Arfvedsonite figures present relationships to the hornblende type, but that species cannot be asserted from them to be in the same isomorphic series with pargasite, for example.

It was thought to be of interest to test further the etching properties of actinolite and hornblende by using caustic alkalis as the solvent instead of hydrofluoric acid. The results were confirmatory of the division just made in the amphiboles. A crystal of Zillerthal actinolite was immersed in molten caustic soda for 15 seconds. A large number of sharply outlined pits were produced on both (110) and (010). Plate I. Figs. 32 and 33 and Fig. 11, are diagrammatic representations of them oriented on their respective planes. Now a cleavage piece of Wolfsberg basaltic hornblende (V. 54) furnished splendid figures on (110) after 35 seconds' exposure in the same reagent, and these were of the varieties shown in Plate I. Figs. 34*a* and 34*b*, and Photograph 16. Another crystal of the Kafveltorp hornblende (V. 42) gave the pits of Plate I. Figs. 35*a*, 35*b*, 35*c*, and Photo. 17, on (110) and pits represented by Figure 12 on (010). Still a third aluminous hornblende (V. 33) from Arendal afforded good figures at 30 seconds, this time practically identical with those of V. 42. Without further analyzing these types, it appears to be a legitimate conclusion that the differing habit of the two may be regarded as significant, not accidental, but indicative of a fundamental difference in the two kinds of substance.

If the tremolite molecule represents one of the fundamental ingredi-



ents in the actinolitic group, the formula of richterite (after Groth, Dana, and Hintze) would have to be recast to show that the latter species is the result of the mixture of $\text{CaMg}_3(\text{SiO}_3)_4$ with another metasilicate molecule. It would be highly interesting to determine the figures on grunerite (FeSiO_3), cummingtonite $[(\text{FeMg})\text{SiO}_3]$, and dannemorite $[(\text{FeMnMg})\text{SiO}_3]$, for purposes of similar comparison; many trials with material of the two former from the classic localities failed to produce figures that could be discussed.

The similarity of the riebeckite pits to those on hornblende may go to show that (if it be true non-aluminous riebeckite that was dealt with during the examination) the strong influence of the alumina molecule may be replaced by that of its common associate, sesquioxide of iron.* In any case, the etch-figures in all thirty of the common and basaltic hornblendes, as well as in the glaucophanes and barkevikite, can hardly be explained except as the effect of an interaction of hydrofluoric acid and a common molecule constituted with reference to one or other or both of the two sesquioxides.

In summary, then, if we accept the law that isomorphic mixtures must have similar etch-figures on corresponding crystallographic planes, we have two divisions among the amphiboles, each of which is isomorphic in itself, but not so related to the other group. If this theory be rejected, we have still the facts remaining of an important difference in the structural plan of each division.

HOLOHEDRAL CHARACTER OF THE MONOCLINIC AMPHIBOLES.

Throughout the whole suite of specimens which I have studied, the evidence is convincing that the family of amphiboles belongs to the holo-

* Haefcke was so impressed with the importance of alumina in the amphibole molecule that he was led to consider it with the other oxides, to be in combination with orthosilicic acid and thus helps to form salts constitutionally different from the non-aluminous amphiboles, the metasilicates (Inaug. Diss. Göttingen, Berlin, 1890). The masterful influence of alumina is further seen in Wiik's table of extinction angles showing the dependence of the angle of extinction of amphiboles on the percentage of Al_2O_3 present. (Zeit. für Kryst., 1882-83, Bd. VII. p. 79.)

That the sum of the sesquioxides as well as the amounts of each should be considered in any comparative study of minerals containing them, is illustrated in an analysis of Doelter's paper on the pyroxenes, in which he traces the influence of alumina and of the sum ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{FeO}$) on the optical constant $c : \epsilon$ of pyroxene (Neues Jahrb. für Min., etc., 1885, Bd. I. p. 43). He finds that FeO alone will not explain the position of ϵ with respect to the vertical axis, nor will Al_2O_3 alone nor Fe_2O_3 alone; but he concluded that both the iron oxides added to the

hedral (Groth's "prismatic") class of the monoclinic system. I examined practically all varieties with this point in mind: figures produced with hydrofluoric acid, caustic soda, caustic potash, and bicarbonate of soda, and the attackability of the different faces, all told the same story. Besides the diagrams so often referred to, I shall introduce another to represent etch-pits on (100) of a hornblende (V. 42) acted upon by caustic soda. (Plate I. Fig. 29.)

COMPARISON WITH THE PYROXENES.

Many years of comparative study, chemical and physical, have evolved a vast body of evidence to restore something of the early belief in the identity of the pyroxene and amphibole substance,* but it is, after all,

alumina furnished a serial correspondence to the variations in $c : c$. If, however, the doubtful case of Mte. Rossi be rejected and it be noted that the extinction $c : c$ for the Siderao occurrence was read on a section not quite parallel to (010), it will be seen that the sum ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) gives better results than any of the variables considered by Doelter. Witness the accompanying table:—

| Locality. | Extinction Angle (010). | $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ | FeO | Fe_2O_3 | Al_2O_3 | $\text{FeO} + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ |
|------------------------|----------------------------|---|------|-------------------------|-------------------------|--|
| | $^{\circ} \quad '$ | % | % | % | % | % |
| Green Augite, Vesuvius | 41 00 | 8.35 | 3.16 | 3.51 | 4.84 | 11.51 |
| Greenwood Furnace | 42 25 | 10.14 | 2.55 | 5.05 | 5.09 | 12.69 |
| Aguas Caldeiras . . | 43 35 | 11.40 | 4.81 | 3.51 | 7.89 | 16.21 |
| Pedra Molar . . . | 45 45 | 11.85 | 5.43 | 6.18 | 5.67 | 17.28 |
| S. Vincent | 46 45 | 13.40 | 5.20 | 5.25 | 8.15 | 18.60 |
| Black Augite, Vesuvius | 46 45 | 14.22 | 4.09 | 4.47 | 9.75 | 18.31 |
| Garza | 47 55 | 14.61 | 5.43 | 4.95 | 9.66 | 20.04 |
| Fassaite (Toald. Foja) | 47 10 | 15.11 | 2.09 | 5.01 | 10.10 | 17.20 |
| Cuglieri | 48 00 | 14.93 | 5.05 | 6.32 | 8.61 | 19.98 |
| Ribiera das Patas . | 51 00 | 22.13 | 5.95 | 7.89 | 14.24 | 28.08 |
| Siderao | 50 05 | 22.37 | 9.14 | 9.29 | 13.08 | 31.51 |
| P. da Cruz | 51 50 | 31.34 | 2.23 | 15.37 | 16.97 | 34.57 |

* Tschermak would find in the relative size of molecule the probable ground for difference in those striking external characters, crystalline development, and cleavage. He hypothecates a size for the amphibole molecule just double that of the pyroxene molecule. Cf. Lehrbuch der Mineralogie, 1894, p. 460.

astonishing to observe the very close parallelism which even a cursory study established between the etching properties of the two mineral genera. This is one part of the present investigation which the author regrets to leave in an especially incomplete stage. Thus, it would be of moment to produce etch-figures on that prism of pyroxene (210), which is nearly equivalent to (110) of amphibole, and compare them with those of the last-mentioned face. This has been left undone for lack of material. But even the facts in hand are wonderfully accordant. To simplify matters, I shall enumerate some of the main conclusions we have reached regarding the etch-pits on amphiboles and note the comparisons with pyroxene in connection with each.

1. Actinolitic amphiboles give one class of etch-pits, aluminous amphiboles another,—especially evident on (010), (110), and (101). I have been able to find a similar strong contrast between diopside and augite in this respect: they were etched on (010) and (110).

2. Not only is such a double cleavage of the groups possible; there are positive similarities in the respective pits on the pinacoids (010) and (100) of the non-aluminous amphibole actinolite and the non-aluminous pyroxene diopside, and there are positive resemblances characterizing the pits on the same planes of augite and hornblende. The paper of Pelikan,* referred to in detail further on, along with those of Wülfing† and Baumhauer‡ show clearly that the etching phenomena (outline of figures, number of pits and of figure-faces, orientation of figures, etc.) on (010) of diopside, using hydrofluoric acid, are hardly distinguishable from those on actinolite. (Compare Photographs 12 and 13.) Pelikan§ has shown, in addition, that the augites from Vesuvius, Laacher See, Wolfsberg, etc., are characterized by only one sort of pit on the clinopinacoid and thus are in contrast to diopside, and, as we now see, are analogous to hornblende. It must be confessed that no amphibole which I have yet etched has yielded anything like so perfect figures on the orthopinacoid as those readily procurable on the same face of Ala diopside (see Photograph 15). While the general resemblance to the pits on (100) of actinolite is certainly great, I cannot say whether or not the pair of figure-faces at the lower end of the diopside pit is represented in the actinolite pit. (Plate I. Fig. 27, is somewhat hypothetical as to the "primary" figure-faces.) I have not been able

* Min. u. petr. Mitth., 1896, Bd. XVI. p. 1.

† Die Pyroxen Familie, Heidelberg.

‡ Poggen. Annalen, Bd. CLIII. p. 75.

§ *Op. cit.*, p. 21.

to secure etchings of this plane for augite nor of (101) for any pyroxene.

3. As was to be expected, the pits on the unit-prism of actinolite and diopside are unlike in outline. I made the experiment of testing the cohesive property of the actinolite substance on a plane making with (010) an angle essentially equal to half the cleavage angle of diopside. A new prism-face was thus ground on a crystal of Zillerthal actinolite, then carefully polished and etched in the usual way, with conc. hydrofluoric acid after two minutes' exposure. The face was found to be covered with etch-hills, the effect of strong attack (much quicker on the artificial face than on any natural face in the prism-zone); but, among them, a few pits which were surprisingly like those on diopside (see Photograph 18), and on aegerine. Further comparison could be made by etching an artificial face on diopside lying $62^{\circ} 15'$ out of the plane of symmetry, and also by using the caustic alkalies in this round of experiment.

4. From the close association of the pyroxenes with our group, it is important to recognise that recently attempts have been made to remove the diopsides from the holohedral class into a hemihedral ("domatische," Groth) class of the monoclinic system. In 1889, G. H. Williams suggested this hypothesis on purely crystallographic grounds, interpreting the imperfect development of the planes about the extremities of the vertical axis of crystals from Orange County, N. Y., and Canaan, Conn., as an evidence of hemihedrism.* In this, he was followed by Dana in the "System" (1892, p. 352). But that the failure of planes about one end of an axis need not mean true structural lack of symmetry is well known, and has lately been exemplified by etch-figures on cuprite that restore it to the holohedral category. Pelikan rightly rejected this argument, but still, on the basis of etching results, he considers it probable that the diopsides are nevertheless hemihedral in Williams's sense.† He was led to this conclusion chiefly by the study of the HF pits on (010). He figures some of these from a Nordmarken specimen which are unsymmetrical in that lines drawn from one side to another through the centre of a pit would not be bisected at that centre; there is, in other words, a lack of that antimetric (dimetric) character necessarily characteristic of (010) if diopside be holohedral. In particular, the asymmetry of the face is supposed to betray itself in the fact that one corner of the rhomboidal figure may be truncated by a fifth figure-face while the oppo-

* Amer. Jour. Science, 1889, Vol. XXXVIII. p. 115.

† *Op. cit.*, p. 19.

site corner is not so truncated. But this phenomenon is a familiar one in etching, as pointed out by Becke with reference to siderite and magnesite; it is simply analogous to the unsymmetrical appearance of a crystal, due to the non-development of faces, which, by the known symmetry of the crystal, should appear on it.* Furthermore, Pelikan states that, even in the typical Ala diopside, the regular antimetric pits appear in abundance, and my own observations on another crystal from the same locality (P. 70, Photograph 13) confirm the statement. There is no trace on my well etched specimen of pits that are not antimetric. Secondly, he uses certain figures on the clinopinacoid of Ala diopside as suggestions of hemihedrism because of the curvature of the edges between their respective figure-faces (see his drawing, *Op. cit.*, p. 20). I have not been able to establish the observation by reference to my Ala specimen, and I am inclined to think the curvature must be a consequence of the solution of planes no longer "primary." If secondary solution really exists, (and the numerous experiments of Becke seem to prove it incontestably,) we should expect it to warp the straight edges between primary figure-faces with some such curves as those represented in Pelikan's drawing.

The evidence seems to be perfectly convincing that diopsides as well as augites, amphiboles as well as pyroxenes, are holohedral, and therefore we may close this brief comparative sketch of their etch-figures.

CRYSTALLOGRAPHIC ORIENTATION OF THE AMPHIBOLES.

The extraordinary resemblance between the amphiboles and pyroxenes in the matter of etch-figures is certainly correlated with likeness in molecular structure, and is an effectual criticism of that mischievous conservatism which has not accepted the arguments of Tschermak, G. H. Williams, and others, in favor of a change in the classic crystallographic orientation of amphibole, introduced by Nordenskiöld. The new differs from the old simply by the rotation of the crystal about the vertical axis

* After these lines had been written, the paper by Baumhauer appeared in the *Zeit. für Kryst.* (1898, Bd. XXX. p. 97), in which the author stated, as the result of a careful examination of some of Pelikan's original material, that, in his opinion, diopside is holohedral, and that the anomalous pits described by Pelikan are really only imperfectly formed representatives of either of the two types of normal antimetric pits, or are the result of the combination or fusion of these two types (*Op. cit.*, p. 101). On similar grounds, Baumhauer regards Colemanite as monoclinic, although certain etch-pits apparently indicate an asymmetric character for the mineral.

by an angle of 180° . The reasons for altering the old orientation have been so well expressed by Williams that they here need no more than mere mention. (1) The base of pyroxene is an important plane on account of the mineral's well known habit of twinning parallel to that face, and, secondly, on account of the (probably resulting) planes of parting that are so often developed parallel to (001). Amphibole shows both phenomena with reference to the unit dome of the old orientation. (2) Parallel intergrowths of the two minerals are much more intelligible if this unit dome of amphibole, sensibly parallel as it is, to the base of the pyroxene, be really regarded as the base of the amphibole. (3) There can be no doubt that the optical and other properties of the two groups can be more easily compared in the new orientation.

Now, when we remember that the pits on (100) are in both families boat-shaped figures with the bow of the boat headed in opposite directions if amphibole be placed in the old orientation, in the same direction if in the new; that the two kinds of pits respectively characteristic of the clinopinacoid on diopside and actinolite are practically identical in arrangement in the new position advocated; that the cohesion relations of the aluminous amphiboles as regards (010) witness to the same close relationship; and that the analogy of the figures on the two sorts of prismatic cleavage is so well brought out in the greater bluntness of the upper end in each case; — it is undeniable that the physico-chemical facts of corrosion with the acid render it highly expedient to follow Dana in his "System," and Lacroix in "La Minéralogie de la France," in reversing, for purposes of systematic comparison, the orientation so recently, and with so little reason, advocated by Hintze.*

OPTICAL ORIENTATION OF AN AMPHIBOLE CRYSTAL OR CLEAVAGE PLATE BY MEANS OF ETCH-FIGURES.

I cannot subscribe to the opinion of Pelikan,† that the etch-pits on the orthopinacoid and on the clinopinacoid of diopside are valueless for purposes of optical orientation. Whether it be because of different methods of procedure or not, yet I have always found a minimum of difficulty in applying Wülfing's directions for the employment of etch-figures to this end. The same facility of use characterizes the corresponding figures on amphiboles. For their actual application, as well as for that of the pits on (110), the reader is referred to the type

* Handbuch für Mineralogie, p. 1186.

† *Op. cit.*, 1896, p. 12.

diagrams and their accompanying descriptions. In every case, there is no doubt which is the upper end of the cleavage piece, on which the (110) etch-pits can be seen. This study of amphiboles was undertaken primarily to determine the value of etch-figures on cleavage pieces, in order to give a means of orienting those belonging to new varieties which are being so often discovered in allotriomorphic development in crystalline rocks. For this reason, I was especially glad to have access to the many species named in the rather voluminous list of page 379. The conclusion is that, while etch-figures render possible a certain amount of differentiation in the whole family of amphiboles, they yet have so much constancy, so many analogies in outline, as to furnish a reliable means of determining up and down, right and left, in a new variety.

ETCH-FIGURES OF ORTHORHOMBIC AND TRICLINIC AMPHIBOLES.

There remain two problems which I have set before me for solution by means of etching; one, the crystal system of anthophyllite and gedrite, the other, the comparison of aenigmatite and monoclinic amphiboles in the matter of cohesions on their prismatic cleavage-faces.

Etch-Figures on Anthophyllite and on Gedrite (110).

With no other amphibole did I find so much difficulty in producing and discussing figures of corrosion as on anthophyllite and its near relative, gedrite. By dint of some patience, however, pits were obtained on (110) that fully served the purpose. The relatively great resistance of these minerals to the solvent power of hydrofluoric acid was illustrated in every specimen. Although recognizable pits could be seen on P. 1, P. 2, and P. 3 at 3 minutes, they were often exceedingly small (longest diameter about equal to 0.002 mm.) and the amount of material removed in solution was insignificant. They could not, however, be much enlarged by longer immersion, as shown by a number of trials at various exposures up to 20 minutes. Instead, they became gradually lost in an indefinite confused surface of irregular solution. The best figures were furnished by P. 2 after 2 minutes' exposure (see Plate I. Fig. 36*a* and 36*b*), most of them were very shallow, elliptical in shape, with the longer axes of the ellipses uniformly parallel to the vertical axis of the crystal; they were commonly aggregated along lines of cleavage. As shown in the diagram, other pits were considerably larger, rectangular, sometimes wholly black under vertical incidence of the light (Plate I. Fig. 36*c*), at other times characterized by several visible

figure-faces (Plate I. Fig. 36*d*). These, like the smaller elliptical pits, possessed one plane of symmetry transverse to the trace of the cleavage, and were, of course contrary to expectation, *sensibly* symmetrical to a plane parallel to the cleavage trace. The other three planes of the unit prism showed figures that clearly indicated the holohedral orthorhombic character of anthophyllite. Gedrite (P. 4 at 8 minutes' exposure) afforded precisely similar phenomena to those of anthophyllite.

These observations confirm the optical determinations of orthorhombic symmetry by Des Cloiseaux, and meet the objection thereto by Hintze,* who referred to the possibility that both anthophyllite and gedrite may really be monoclinic, but imitate the optical behavior of an orthorhombic mineral. That these minerals are monoclinic for chemical reasons has more recently been suggested by Retgers:† we have once again an illustration of how etch-figures may come to the help of the chemical theorist.

In passing, it may be noted that the plane of easy parting (010) in hypersthene (P. 69) and bronzite (P. 67 and P. 68) gave with hydrofluoric acid extremely sharp pits with six-sided bisymmetric outline, that betokened orthorhombic symmetry for these minerals, though I could obtain no certain results on etching (110).

*Etch-Figures on the Prismatic Cleavages (110) and (110)
of Aenigmatite.*

Without destroying the splendid crystals of aenigmatite which Mr. Ussing was good enough to place at my disposal, I was able to etch and orient cleavage pieces of that mineral. The crystals showed (Brögger's orientation) the planes (110), (110), (010), (151). The standard conditions of etching were again used, and, after some trouble, both cleavages were finally attacked with successful outcome. Figure 13 and Plate I. Fig. 37*a* will give an idea of the pits. They are triangular in outline, very analogous to the pits on the cleavage of common hornblende, but with a decided peculiarity of orientation. The attitude of the figure-faces shows a greater resistance to attack in a direction parallel to the edge 110 : 110 than at right angles to it, a phenomenon we have already noticed in treating of the analogous position of the caustic soda figures on arfvedsonite.‡ Neighboring pits may overlap, and thus the figure-faces

* Handbuch, p. 1180.

† Zeit. für phys. Chemie, 1895, Bd. XVI. p. 618.

‡ Baumhauer observed the independence of etch-figures and cleavage in the case of several species. Pogg. Annalen, 1872, Bd. CXLV. p. 460.

which are nearly parallel to the trace of the second cleavage may run into one another, forming a more or less straight edge in that direction (Plate I. Fig. 37*b*). The small differences in the shape and orientation

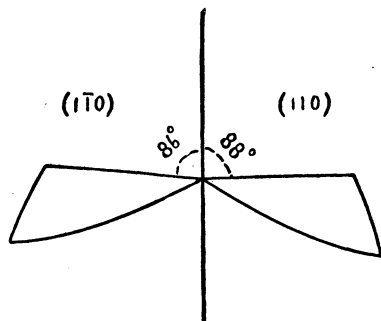


FIGURE 13.

of the pits on (110) and ($1\bar{1}0$) are such as to form another testimony to the fact expressed by Förstner that cossyrite (aenigmatite) closely approximates a monoclinic habit.* (See Figure 13.)

It is possible that the moot question as to whether kölbingtonite is a distinct species, or (after Brögger) an intergrowth of arfvedsonite and aenigmatite, might be settled by etching cleavage pieces of the mineral.

Zinc-bearing rhodonite (fowlerite, P. 72) is much nearer the monoclinic pyroxenes, as shown by etch-figures, than is aenigmatite like the monoclinic amphiboles. Fowlerite at 45 seconds' exposure gave triangular pits on (110) and ($1\bar{1}0$), which are elongated in the sense of the edge 110 : $1\bar{1}0$, and are strongly suggestive of the pyroxene figures on cleavage plates.

SUMMARY OF CONCLUSIONS.

Reviewing the ground over which we have come, we may make the following brief *résumé* of results:—

(1) It seems to be clear that, for the group of the amphiboles, a special *method* of etching must be adopted, if a comparative study of the etch-figures derived from the different species is to be instituted. A universal solvent must, of course, be used, but its temperature, degree of concentration, and facility of convection at the time of each attack must be attended to if a strict control over the effects of corrosion be possible. It is only by observing this principle, that the measurement of the outlines of pits and their elements of form will lead to the most valued conclusions; and we have seen that measurement, i. e. discussion of the figures by quantitative methods, serves this purpose much more perfectly than does a mere statement of the *kind* of pit or etch-hill to be seen on any given specimen. It has further been shown, with respect to the pits

* Zeit. für Kryst., Bd. V. p. 350.

on the cleavages and on the clinopinacoid of amphibole at least, that the action of hydrofluoric acid is seriously affected by its mixture with pure water and also seriously affected, in the opposite sense, by its mixture with sulphuric acid; the action of pure hydrofluoric acid gas is intermediate to that of both kinds of mixture. Is it not *always* necessary to guard the conditions of attack when etching of crystals by chemical corrosion is to be the means of comparison among the substances represented thus in the crystalline state?

The relatively rapid process of studying etch-figures in vertically incident light can, under the circumstances just outlined, lead to results of importance, not inferior to that attaching to problems where the rather laborious method of determining the exact symbols of figure-faces by means of the goniometer and the Brewster light-figures is necessary.

(2) A scale of optimum exposures for (110) under standard conditions is recorded and the attempt is made to systematize the amphiboles as regards their attackability on the same face. The comparative attackability by hydrofluoric acid of the different faces on certain non-aluminous amphiboles has been determined. It has been found that this property is affected, in large measure, by the physical state of the specimen attacked.

(3) In many instances it has been exemplified that a systematic comparison of etch-figures on different species will be of most service if the observer recognizes the principle that there is a decided change in the etch-pit characteristic of any face, in accordance with the stage it has reached in the process of *maturing* from an initial figure to the often very different figure peculiar to an advanced stage of corrosion. Chiefly for this reason, it has been found difficult, if not impossible, to tell which of the many successive figure-faces composing a given pit on amphibole are the "primary" figure-faces of Becke's definition. It may have been, too, partly for this reason, that I have found it as yet impossible to co-ordinate perfectly the figure-faces and the related directions of easy and difficult solution, so as to construct the "Lösungsoberfläche" characterizing any amphibole.

(4) The curious adventitious etch-hills on hornblende, illustrated in Photograph 12, have led us to suspect that they in no wise represent the true cohesional property of the face considered, but have suggested the hypothesis (following Becke) that they may be due to the unequal protection of the mineral surface by the solid products of the chemical reaction, and that the parts so shielded from attack will project above the general surface after corrosion has further advanced. It would be

interesting to know if other studies of etch-hills will confirm this hypothesis.

(5) A point of considerable theoretical interest is raised by the behavior of the clinopinacoid of actinolite when etched by hydrofluoric acid. It is another of those puzzling cases of the existence, side by side, on the same face, of two quite different kinds of figures, an association for which valid explanation has not yet been vouchsafed.

(6) The amphibole family merits particular notice from the student of etch-figures because it forms a test case for the theory that isomorphic crystalline bodies must have similar etch-figures on corresponding faces. If actinolite and common hornblende, for example, be isomorphous, then their etch-pits must be "similar" in a sense very different from that adopted in the foregoing paper. By our usage, they can only be said to be "analogous." In view of these facts, if this theory of the association of isomorphism and etchings be of universal application, it will be necessary to define more closely than has yet been done by an advocate of the theory, the degree of variability that may occur in the etch-figures of any isomorphous series.

(7) The amphiboles are throughout holohedral.

(8) A further proof of the extraordinary similarity between the pyroxene substance and the amphibole substance is afforded by the study of the pits on crystals showing (010), (100), and (110). This is especially true of the phenomena which can be observed when the clinopinacoid is, in each case, etched with hydrofluoric acid.

(9) It is incontestable that, in spite of their different crystalline development and angles of cleavage, pyroxene and amphibole are so closely and so instructively allied that the standard orientation for both should bring out as conveniently as possible their points of resemblance. Taking etchings as particularly significant of what there be of genuine likeness in the two kinds of substance, there can be no doubt that the orientation proposed by Tschermak should be universally adopted in preference to the older orientation.

(10) It is further possible to make etch-figures on amphibole of practical value by using them as a means of orienting cleavage flakes and other crystal fragments. This use is parallel to that proposed by Wülfing for the pyroxenes.

(11) Lastly, so far as etch-figures may be trusted to show relationships, we have the following results of our survey as to the systematic classification of the amphiboles.

The patent pronounced separation between non-aluminous and alumi-

nous amphiboles, signalized by the two-group division of all our handbooks, is once more confirmed. At the same time, attention has been again called to the overwhelming importance of a sesquioxide, whether iron oxide or alumina, in the mineral.

Glaucophane and gastaldite are the same species, and both isomorphous with hornblende.*

Arfvedsonite appears to hold a more or less independent place in the family of amphiboles.

Barkevikite is more closely related to common hornblende than to arfvedsonite.†

Anthophyllite and gedrite are plainly orthorhombic and holohedral.

Aenigmatite diverges considerably from the amphibole habit, but betrays a tendency toward symmetrical cohesion property, as it does toward crystallographic symmetry.‡

Lastly, it is believed that our present methods of determination of species can be reinforced by the detailed study of mineral groups with respect to etching. The peculiarities of the pits on the cleavages of riebeckite, arfvedsonite, and barkevikite make it easy to say to which of these a given cleavage flake belongs. Similarly, the differentiation of crossite and glaucophane, difficult as it often is by purely optical methods, is ready at hand if the mineral be etched on (110). The striking characteristics of the Philipstad hornblende (V. 101) first became evident in the process of etching cleavage pieces. Its description as a new variety will form the sequel to this paper.

* Cf. Strüver's statement: "It is probable that glaucophane and gastaldite are isomorphous with amphibole [proper], but it is not yet *proved*." Neues Jahrb. für Min., etc., 1887, Bd. I. p. 217.

† The same opinion is held by Lacroix, chiefly on optical grounds (Minéralogie de la France, Tom. I. p. 561); the opposite opinion by Brögger (Zeit. für Kryst., Bd. XVI. p. 414), followed by Dana (System, p. 403), and Hintze (Handbuch, p. 1256).

‡ See Brögger, *op. cit.*, p. 424.

PLATE I.

Fig.

1. Initial form of pit, Actinolite type (110), HF. $\times 300$.
2. Mature pit of the Actinolite type (110), HF. $\times 300$.
3. Another form of the mature pit of the Actinolite type (110), HF. $\times 300$.
4. A rather exceptional variant on the normal Actinolite type (110), distinguished by a well defined fourth figure-face at the lower end, HF. $\times 300$.
5. Initial form of the Wolfsberg sub-type (110), HF. $\times 1800$.
6. The Wolfsberg sub-type (110), HF. $\times 300$.
7. Compound stepped etch-pit of the Wolfsberg sub-type (110), HF. $\times 300$.
8. Exceptional pit of the Wolfsberg sub-type, showing a fourth figure-face at the lower end (110), HF. $\times 300$.
9. Immature pit of the Kragerö sub-type (110), HF. $\times 300$.
10. Matured pit of the Kragerö sub-type (110), HF. $\times 300$.
11. Another form of the last on another Hornblende variety, showing the common occurrence of a fourth figure-face at the lower end of the pit. $\times 300$.
12. An exceptional pit found on (110), along with the pits of Figure 11. $\times 300$.
13. The Edenville sub-type (110), HF. $\times 600$.
14. Another form of the last, where the individual figure-faces can no longer be distinguished. $\times 600$.
- 15 and 16. Two forms of the Glaucophane type (110), HF. $\times 600$.
17. The Crossite type (110), HF. $\times 1000$.
- 18 and 19. Two forms of the Riebeckite type (110), HF. $\times 1000$.
20. The type of pit on Barkevikite (110), HF. $\times 300$.
- 21 and 22. Two forms of the pits on Arfvedsonite (110), HF. $\times 175$.
- 23a, 23b, 23c. Pits on (010) of Actinolite, HF. 23a is the "light" etch-pit, the other two the "dark" pits simultaneously occurring with the first, HF. $\times 300$.
24. The modification of the normal pit on Actinolite (110) by the admixture of 5% sulphuric acid to the commercial hydrofluoric acid generally used. $\times 300$.
- 25a and 25b. The same as the last, except that the admixture is here 50% of sulphuric acid. $\times 300$.
26. The type of pits on (010) of common and basaltic (aluminous) Hornblendes, HF. $\times 300$.
27. A pit on (100) of Actinolite (non-aluminous amphibole), HF. $\times 300$.
28. A pit on (100) of basaltic Hornblende (aluminous), HF. $\times 300$.
29. Caustic soda pit on (100) of basaltic Hornblende. $\times 300$.
30. Pit on ($\bar{1}01$) of basaltic Hornblende, HF. $\times 600$.
31. Pit on ($\bar{1}01$) of Actinolite and other non-aluminous amphiboles, HF. $\times 300$.
- 32 and 33. Caustic soda pits on Actinolite (110). $\times 1200$.
- 34a and 34b. Caustic soda pits on basaltic Hornblende (110). $\times 300$.
- 35a, 35b, and 35c. Caustic soda pits on the Kafveltorp Hornblende (110). $\times 600$.
- 36a, 36b, 36c, and 36d. The various types of pits produced on Anthophyllite and Gedrite, (110), HF. $\times 3000$.
- 37a and 37b. Pits on Aenigmatite (110), HF. $\times 3000$.

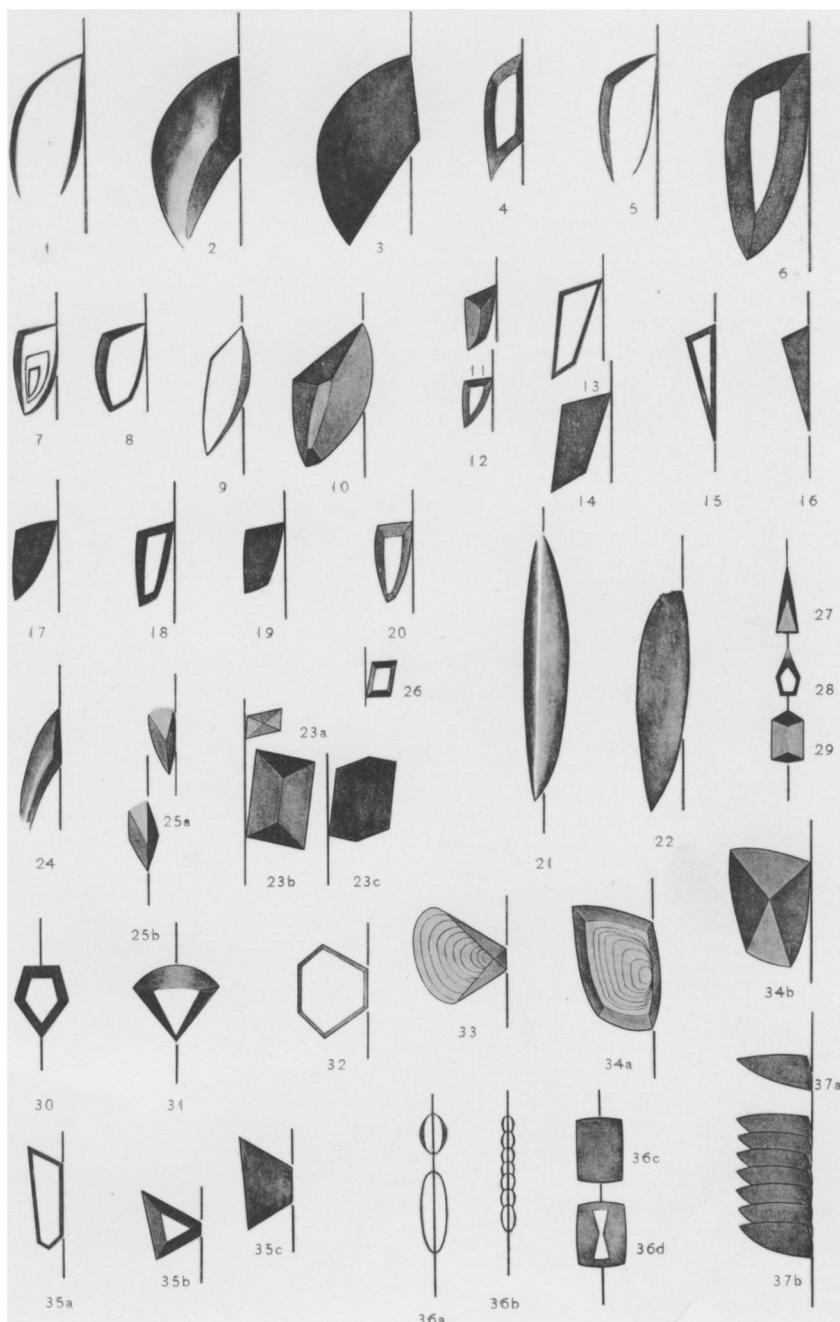


PLATE II.

DESCRIPTION OF THE MICROPHOTOGRAPHS.

Etch-figures are illustrated as follows : —

- No. 1. Actinolite type on (110), Zillerthal Actinolite, HF. $\times 88$.
- No. 2. Kragerö sub-type on (110), Kragerö Hornblende, HF. $\times 78$.
- No. 3. The same on another variety, Kafveltorp Hornblende. $\times 78$.
- No. 4. Philipstad sub-type on (110), (crystal face = outer zone), showing pits with blunted lower end, Philipstad Hornblende, HF. $\times 225$.
- No. 5. The same on another crystal, showing pits characterized by a sharpening of the lower end. $\times 95$.
- No. 6. Philipstad sub-type on (110), (one form on the cleavage surface of the inner zones,) Philipstad Hornblende, HF. $\times 225$.

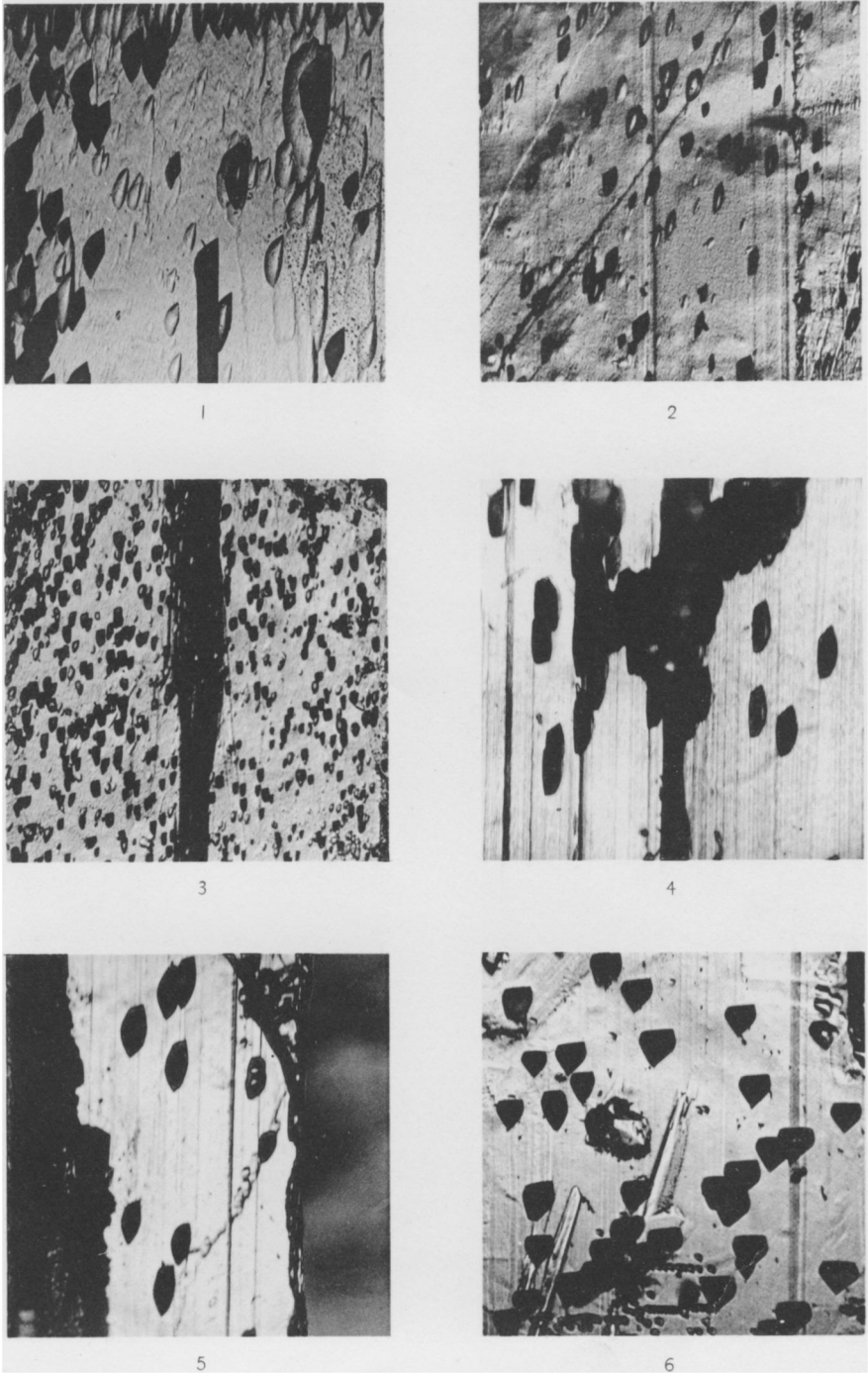
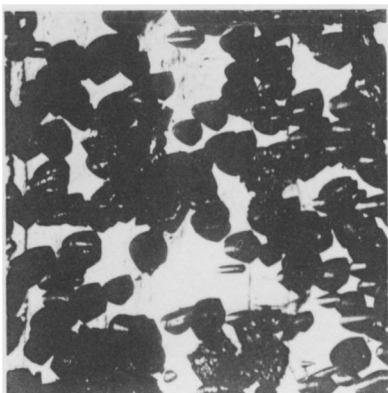


PLATE III.

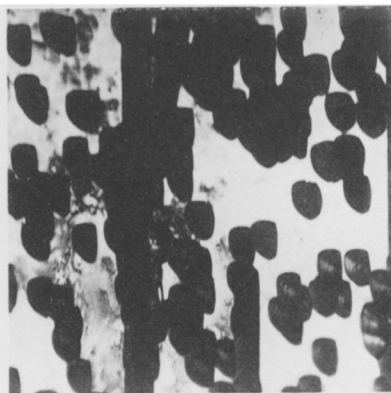
DESCRIPTION OF THE MICROPHOTOGRAPHS.

Etch-figures are illustrated as follows : —

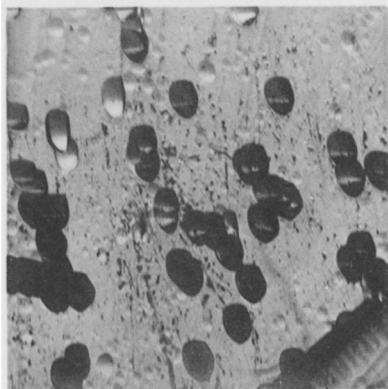
- No. 7. The same as No. 6 on another crystal, showing the common distortion of the pits, HF. $\times 78$.
- No. 8. Caustic soda pits on Philipstad Hornblende (110), (crystal face). $\times 225$.
- No. 9. Caustic soda pits on Philipstad Hornblende (110), (cleavage, inner zones). $\times 225$.
- No. 10. Etch-hills on (110), basaltic Hornblende from Mayenegg (HF gas). $\times 71$.
- No. 11. Pits on (110), Arfvedsonite from Kangerdluarsuk, HF. $\times 78$.
- No. 12. Pits on (010), Zillerthal Actinolite, HF. $\times 78$.



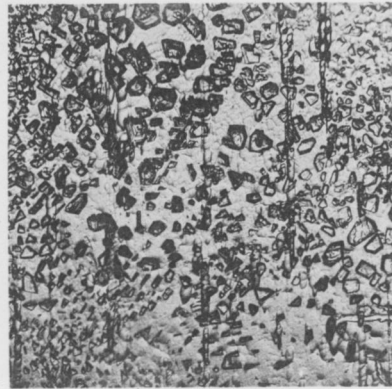
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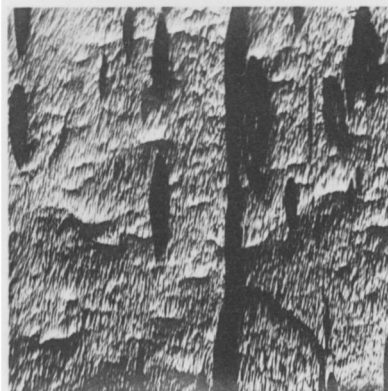
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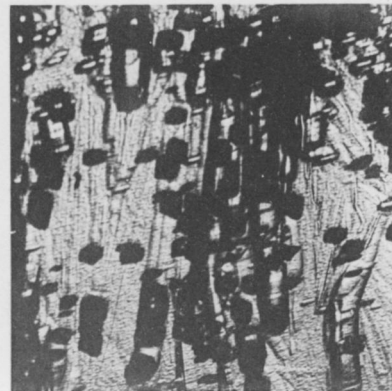
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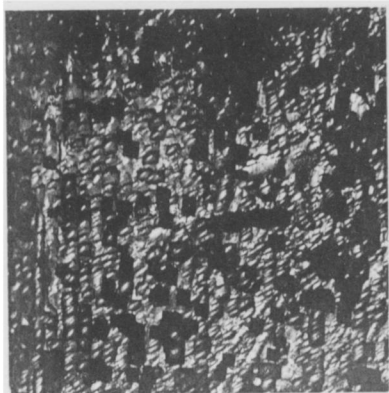
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PLATE IV.

DESCRIPTION OF THE MICROPHOTOGRAPHS.

Etch-figures are illustrated as follows :—

- No. 13. Pits on (010), Ala Diopside, HF. $\times 78$.
- No. 14. Pits on (010), basaltic Hornblende from Kafveltorp, HF. $\times 78$.
- No. 15. Pits on (100), Diopside from Ala, HF. $\times 78$.
- No. 16. Caustic soda pits on (110), Wolfsberg basaltic Hornblende. $\times 78$.
- No. 17. Caustic soda pits on (110), basaltic Hornblende from Kafveltorp.
 $\times 225$.
- No. 18. Pits on (110), Diopside from Ala, HF. $\times 78$.



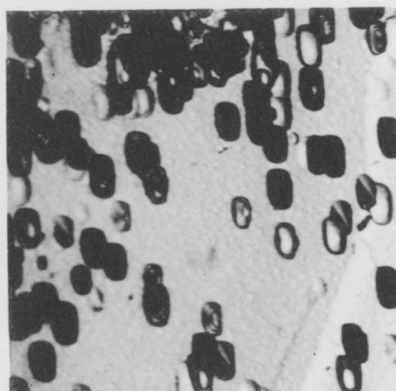
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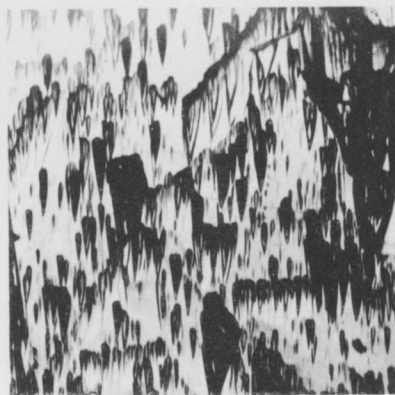
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